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PRACTICE PAPERS 2018

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CHEMISTRY MUSING

CONCEPT MAP

CONCEPT BOOSTER

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CHEMISTRY MUSING

PROBLEM SET 56

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material.
In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.
The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET

1. A hydrogen electrode placed in a buffer solution of NaCN and HCN in the ratio $x : y$ and $y : x$ has electrode potential values a and b volts respectively, at 25 °C. If the difference $(a - b)$ is 35.52 mV, the ratio $y : x$ is
(a) 2 (b) 3/2 (c) 3 (d) 2/3

2. The normal boiling points of four elements with consecutive atomic numbers are tabulated as :

Elements	W	X	Y	Z
Atomic number	N	$N+1$	$N+2$	$N+3$
Boiling point (°C)	58	–152	688	1380

One of the important ore of Z is celestine then, which of the following compounds would be the most stable?
(a) W_2X (b) W_2Y (c) W_2Z (d) XY_2

3. An amine on treatment with HNO_2 evolved N_2 gas. The amine on exhaustive methylation with CH_3I formed a quaternary salt containing 59.07% iodine. The amine is likely to be
(a) CH_3NH_2 (b) $(CH_3)_2NH$
(c) $C_2H_5NH_2$ (d) $(CH_3)_3N$

4. For the given reaction,
$$HO-CH_2-CH_2-CH_2-CH_2Cl \xrightarrow{\bar{O}H} (A)$$
which of the following statements is true?
(i) (A) is butane-1, 4-diol.
(ii) (A) is tetrahydrofuran.
(iii) (A) is prepared by S_N1 reaction.
(iv) (A) is prepared by intramolecular S_N2 reaction.
(a) (i) only (b) (ii) and (iv) only
(c) (i) and (iv) only (d) (ii) and (iii) only

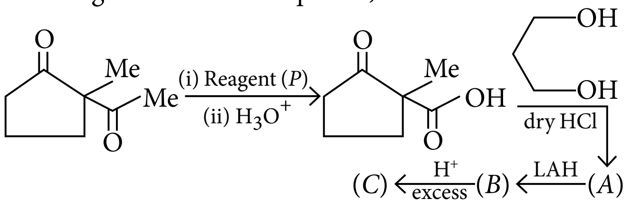
5. Ordinary strong solutions of HCl, HNO_3 and H_2SO_4 contain roughly
(a) 1/5, 2/3 and 3/3 fractions of pure acid in water respectively
(b) 2/3, 1/5 and 3/3 fractions of pure acid in water respectively
(c) 2/3, 3/3 and 1/5 fractions of pure acid in water respectively
(d) none of these.

JEE ADVANCED

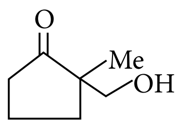
6. A given sample of milk turns sour at room temperature (20 °C) in 64 hours. In a refrigerator at 3 °C, milk can be stored three times as long before it sours. How long will it take milk to sour at 40 °C?
(a) 192 hr (b) 64 hr (c) 20.5 hr (d) 30 hr

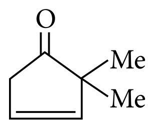
COMPREHENSION

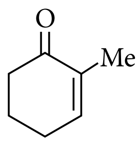
For the given reactions sequence,

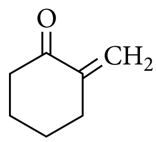


7. reagent (P) is
(a) $Br_2/\bar{O}H$ (b) NaOI
(c) $Ca(OH)_2 + Cl_2$ (d) all of these.

8. compound (C) is
(a) 

(b) 

(c) 

(d) 

INTEGER VALUE

9. For how many of the following, the apparent weight increases by applying magnetic field? NO, NO_2, O_2, $K_3[Fe(CN)_6]$, KO_2, $MnSO_4$, $NiSO_4$, $CuSO_4$, $ZnSO_4$

10. During the electrolysis of conc. H_2SO_4, it was found that $H_2S_2O_8$ and O_2 were liberated in a molar ratio of 3 : 1. If moles of H_2 in terms of moles of $H_2S_2O_8$ is $a : b$ then the value of $3 \times a/b$ is

JEE Advanced

Exam on 20^{th} May

PRACTICE PAPER 2018

PAPER - I

SECTION 1 (MAXIMUM MARKS : 28)

- *This section contains SEVEN questions.*
- *Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four options is (are) correct.*
- *For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.*
- *For each question, marks will be awarded in one of the following categories :*

  Full Marks : +4 *If only the bubble(s) corresponding to all the correct option(s) is(are) darkened.*

  Partial Marks : +1 *For darkening a bubble corresponding to each correct option, provided NO incorrect option is darkened.*

  Zero Mark : 0 *If none of the bubbles is darkened.*

  Negative Marks : –2 *In all other cases.*
- *For example, if (a), (c), and (d) are all the correct options for a question, darkening all these three will get +4 marks; darkening only (a) and (d) will get +2 marks; and darkening (a) and (b) will get–2 marks, as a wrong option is also darkened.*

1. A mixture of two inorganic salts gives following chemical reactivity :

(i) Mixture on reaction with dilute H_2SO_4 produces a colourless and unpleasant gas which turns acidified potassium dichromate paper green.

(ii) Mixture on reaction with concentrated H_2SO_4 gives reddish brown gas which does not produce orange red spots on starch paper.

(iii) The mixture gives white precipitate with barium chloride solution which is soluble in dilute HCl.

(iv) The sodium carbonate extract of mixture responds to brown ring test.

The mixture contains

(a) SO_3^{2-} and NO_3^- anions

(b) S^{2-} and NO_3^- anions

(c) SO_3^{2-} and NO_2^- anions

(d) SO_3^{2-} and Br^- anions.

2. From the following data, mark the option(s) where ΔH is correctly written for the given reaction.

Given : $H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$; $\Delta H = -57.3$ kJ/mol

$\Delta H_{solution}$ of $HA_{(g)} = -70.7$ kJ/mol

$\Delta H_{solution}$ of $BOH_{(g)} = 20$ kJ/mol

$\Delta H_{ionisation}$ of HA = 15 kJ/mol and BOH is a strong base.

Reaction	$\Delta_r H$**(kJ/mol)**
(a) $HA_{(aq)} + BOH_{(aq)} \longrightarrow BA_{(aq)} + H_2O$	–42.3
(b) $HA_{(g)} + BOH_{(g)} \longrightarrow BA_{(aq)} + H_2O$	–93
(c) $HA_{(g)} \longrightarrow H^+_{(aq)} + A^-_{(aq)}$	–55.7
(d) $BOH_{(g)} \longrightarrow B^+_{(aq)} + OH^-_{(aq)}$	–20

3. The hemiacetal form of glucose is indicated by

(a) reaction with $(CH_3CO)_2O$

(b) oxidation with Tollens' reagent

(c) reduction with HI/P

(d) glycoside formation.

4. $MeCOOEt \xrightarrow[\text{(ii) } HNO_2,\ \text{(iii) } OH^-]{\text{(i) } NH_2NH_2} (B) \xrightarrow{MeOH} (C)$

Which of the following statements are correct about the given reactions sequence?

(a) The compounds (B) and (C), respectively, are $Me-N=C=O$ and MeNHCOOMe.

(b) The compounds (B) and (C), respectively, are $Et-N=C=O$ and $MeNH_2$.

(c) The reaction proceeds via the formation of acyl nitrene ($MeCO\ddot{N}$:) as the intermediate species.

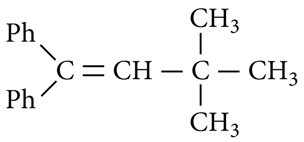
(d) The reaction proceeds via the formation of acyl nitrene ($EtCO\ddot{N}$:) as the intermediate species.

5. Which of the following substrates will give rearranged product in hydration reaction?

(a) $CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH=CH_2$

(b) $CH_3-\underset{\cdot\cdot}{\ddot{S}}-CH_2-CH=CH_2$

(c) $CH_3-CH=CH_2$

(d) 

6. Identify compound(s) in which gauche conformer is more stable than staggered.
(a) 1, 2-Difluoroethane (b) Chloropropane
(c) Ethylene glycol (d) Succinic acid

7. Which among the following statements is/are correct?
(a) XeF_4 and SbF_5 combine to form salt.
(b) He and Ne do not form clathrates.
(c) He has lowest b.pt. in its group.
(d) He diffuses through rubber and polyvinyl chloride.

SECTION 2 (MAXIMUM MARKS : 15)

- *This section contains FIVE questions.*
- *The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive.*
- *For each question, darken the bubble corresponding the correct integer in the ORS.*
- *For each question, marks will be awarded in one of the following categories :*

Full Marks : +3 *If only the bubble corresponding to the correct answer is darkened.*
Zero Marks : 0 *In all other cases.*

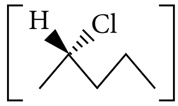
8. Number of chelate rings in $[Cr(ox)_3]^{3-} = a$
Number of chelate rings in $[Co(en)(NH_3)_2(py)_2]^{3+} = b$
Number of chelate rings in $[Fe(EDTA)]^- = c$
Number of chelate rings in brown ring complex $[Fe(H_2O)_5(NO)]SO_4 = d$
then the value of $(a + b + c + d)$ is

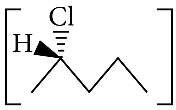
9. If edge fraction unoccupied in ideal anti-fluorite structure is x. Calculate the value of Z $\left(\text{where, } Z = \dfrac{x}{0.097}\right)$.

10. m-Phenylenediamine when treated with $NaNO_2$ and HCl at 0-5 °C undergoes self-coupling reaction to produce a trimer, known as Bismarck brown. The total number of nitrogen atoms in the final product is

11. A decapeptide (mol. wt. 796) on complete hydrolysis gives glycine, alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is

12. When (S)-2-chloropentane reacts with NaOH in 75 per cent ethanol and 25 per cent acetone follows rate law :

Rate = 2.35×10^{-5}  $[OH^-]$ +

3.0×10^{-6} 

What will be percentage of S_N1 product when concentration of $[OH^-] = 1.5$ molar?

SECTION 3 (MAXIMUM MARKS : 18)

- *This section contains SIX questions of matching type.*
- *This section contains TWO tables (each having 3 columns and 4 rows)*
- *Based on each table, there are THREE questions*
- *Each question has FOUR options (a), (b), (c) and (d). ONLY ONE of these four options is correct*
- *For each question, darken the bubble corresponding to the correct option in the ORS*
- *For each question, marks will be awarded in one of the following categories :*

Full Marks : +3 *If only the bubble corresponding to the correct option is darkened.*
Zero Marks : 0 *If none of the bubbles is darkened*
Negative Marks : –1 *In all other cases.*

Answer Q. 13 to 15 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contain number of moles, volumes at STP and number of atoms, respectively.

Column 1	Column 2	Column 3
(I) 0.125	(i) 7840 mL	(P) 13.25×10^{23}
(II) 0.35	(ii) 11.2 dm^3	(Q) 6.32×10^{23}
(III) 1.1	(iii) 2.8 L	(R) 6.023×10^{23}
(IV) 0.50	(iv) 24640 cc^3	(S) 3.011×10^{23}

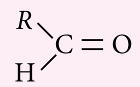
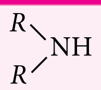
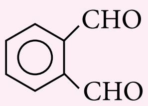
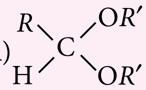
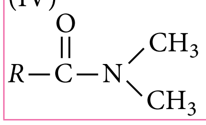
13. The correct combination for 16 g of NO_2 is
(a) (I) (ii) (R) (b) (II) (iii) (S)
(c) (II) (i) (Q) (d) (IV) (iii) (P)

14. Oxygen gas occupies 10.5 L at 27 °C under a pressure of 2.5 atm. At STP correct match for the sample will be
(a) (IV) (ii) (R) (b) (III) (iv) (P)
(c) (II) (i) (Q) (d) (I) (iii) (S)

15. For 32 g of sulphur, correct combination will be
(a) (I) (ii) (P) (b) (I) (iii) (R)
(c) (II) (iii) (Q) (d) (III) (iv) (S)

Answer Q. 16 to 18 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contain reactants, intermediates and products, respectively.

Column 1	Column 2	Column 3
(I) 	(i) γ-Hydroxy acid	(P) 
(II) $RCONH_2$	(ii) Hemiacetal	(Q) 1°-amine
(III) 	(iii) Alkyl isocyanate	(R) 
(IV) 	(iv) Carbene	(S) Phthalide

16. Correct matching for addition of $R'—OH$ will be
(a) (I) (iii) (S)
(b) (I) (ii) (R)
(c) (III) (ii) (P)
(d) (III) (i) (Q)

17. Correct matching for intramolecular Cannizzaro reaction will be
(a) (III) (ii) (P)
(b) (IV) (iii) (R)
(c) (III) (i) (S)
(d) (I) (iv) (Q)

18. Correct matching for Hoffmann bromamide degradation reaction is
(a) (IV) (iii) (Q)
(b) (IV) (iv) (P)
(c) (II) (i) (R)
(d) (II) (iii) (Q)

PAPER - II

SECTION 1 (Maximum Marks : 21)

- *This section contains SEVEN questions.*
- *Each question has FOUR options (a), (b), (c) and (d). ONLY ONE of these four options is correct.*
- *For each question, darken the bubble corresponding to the correct option in the ORS.*
- *For each question, marks will be awarded in one of the following categories :*
  Full Marks : *+3 If only the bubble corresponding to the correct option is darkened.*
  Zero Marks : *0 If none of the bubbles is darkened.*
  Negative Marks : *–1 In all other cases.*

1. For a 3*s*-orbital, $\psi(3s) = \frac{1}{9\sqrt{3}}\left(\frac{1}{a_0}\right)^{1/2}(6 - 6\sigma + \sigma^2)e^{-\sigma/2}$

where, $\sigma = \frac{2Zr}{3a_0}$. What is the maximum radial distance of node from nucleus?

(a) $\frac{2}{3}\frac{(3+\sqrt{3})a_0}{Z}$
(b) $\frac{3}{2}\frac{(3+\sqrt{3})a_0}{Z}$
(c) $\frac{3}{2}\frac{(3-3\sqrt{3})a_0}{Z}$
(d) $\frac{3}{2}\frac{(3-\sqrt{3})a_0}{Z}$

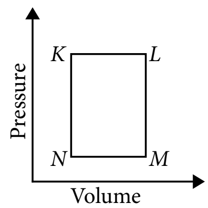
2. In first order reaction, $A \longrightarrow B$, A is optically active and B is optically inactive. A series of experiments were conducted on a solution of A :

Time	0	60 min	∞
Optical rotation	82°	77°	2°

Assume some impurity is present, calculate the optical rotation after 5 hours.

(Given ln 1.066 = 0.064, $e^{0.32} = 1.377$)
(a) 60
(b) 30
(c) 20
(d) 120

3. A fixed mass '*m*' of a gas is subjected to transformation of states from *K* to *L* to *M* to *N* and back to *K* as shown in the figure :



The pair of isochoric processes among the transformation of states is
(a) *K* to *L* and *L* to *M*
(b) *L* to *M* and *N* to *K*
(c) *L* to *M* and *M* to *N*
(d) *M* to *N* and *N* to *K*.

4. Devise a series of reactions to convert ethyl 3-oxobutanoate to ethyl 4-oxopentanoate. Select reagents and conditions from the following table, listing them in the order of use :
(1) Sodium ethoxide in ethanol
(2) Ethanol + Acid catalyst
(3) H_3O^+; heat
(4) CO_2 then H_3O^+
(5) Mg in ether
(6) PBr_3
(7) $NaBH_4$ in alcohol
(8) CH_2I_2 in ether; Zn – Cu
(9) $BrCH_2COOC_2H_5$
(10) $(CH_3CO)_2O$; Pyridine
(a) 1, 9, 3 then 2
(b) 7, 6, 5, 10 then 2
(c) 3, 7, 6, 5, 10 then 2
(d) 8, 3 then 2

5. FeO crystal has a simple cubic structure and each edge of the unit cell is 5 Å. Taking density of the oxide as 4 g/cc, the number of Fe^{2+} and O^{2-} ions present in each unit cell are
(a) $4Fe^{2+}$ and $4O^{2-}$ (b) $6Fe^{2+}$ and $6O^{2-}$
(c) $2Fe^{2+}$ and $2O^{2-}$ (d) $1Fe^{2+}$ and $1O^{2-}$

6. The bond angle between two hybrid orbitals is 180°. The percentage *s*-character of hybrid orbital is
(a) 50 (b) 75
(c) 33 (d) 66

7. What is the complementary RNA sequence for the DNA segment AATCAGTT?
(a) AAUCAGUU (b) CCAUCGAA
(c) AACUGAUU (d) UUAGUCAA

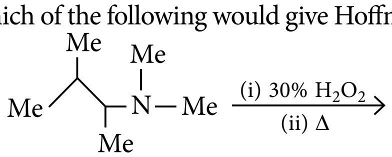
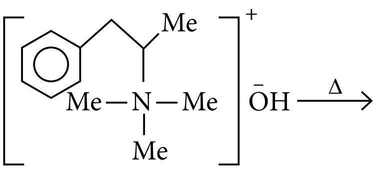
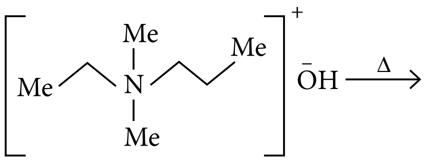
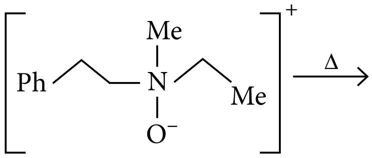
SECTION 2 (MAXIMUM MARKS : 28)

- *This section contains SEVEN questions.*
- *Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct.*
- *For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.*
- *For each question, marks will be awarded in one of the following categories :*

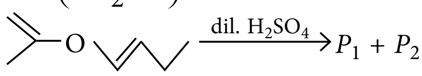
Full Marks : + 4 *If only the bubble(s) corresponding to all the correct option(s) is(are) darkened.*
Partial Marks : +1 *For darkening a bubble corresponding to each correct option, provided NO incorrect option is darkened.*
Zero Marks : 0 *If none of the bubbles is darkened.*
Negative Marks : –2 *In all other cases.*

- *For example, if (a), (c), and (d) are all the correct options for a question, darkening all these three will get +4 marks; darkening only (a) and (d) will get +2 marks; and darkening (a) and (b) will get –2 marks, as a wrong option is also darkened.*

8. Which statements are correct about lactose?
(a) $(C_1 - \beta)$ (OH) of glucose is linked with (C_4—OH) of galactose.
(b) $(C_1 - \beta)$ (OH) of galactose is linked with (C_4—OH) of β-glucose.
(c) It is hydrolysed both by amylase and lactase.
(d) It exhibits mutarotation.

9. Which of the following would give Hoffmann alkene?
(a) 
(b) 
(c) 
(d) 

10. Select the correct statement(s).
(a) On Pauling scale, the difference in *EN* of two atoms *A* and *B* in SI units is
$(EN_A - EN_B) = 0.1017\sqrt{\Delta_{A-B}}$
(b) On Pauling scale, the difference in *EN* of two atoms *A* and *B* in kcal mol^{-1} is
$(EN_A - EN_B) = 0.208\sqrt{\Delta_{A-B}}$
(c) The Mulliken's *EN* values are scaled down to match the Pauling value by dividing $\left(\frac{IP + EA}{2}\right)$ in eV by 2.8
(d) The Mulliken's *EN* values are scaled down to match the Pauling value by multiplying $\left(\frac{IP + EA}{2}\right)$ in eV by 3.17

11. 
P_1 and P_2 products are identified by
(a) Tollens' reagent (b) Iodoform test
(c) $Br_2 + H_2O$ test (d) 1% of alkaline $KMnO_4$.

12. Mark the incorrect statement(s).
(a) Potassium dichromate oxidises a secondary alcohol into a ketone.
(b) Potassium permanganate is a weaker oxidising agent than potassium dichromate.
(c) Potassium dichromate oxidises a secondary alcohol into aldehyde.
(d) Alkaline $KMnO_4$ solution oxidises tertiary alcohol to a mixture of a ketone and an acid.

13. Select the correct statement(s).
(a) Chelation effect is maximum for five or six membered rings.
(b) Complex ions in which ligands can be interchanged rapidly are said to be non-labile.
(c) For a given ion and ligand, greater the charge on the metal ion, greater is the stability.
(d) $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ can be distinguished by magnetic moment.

14. Which of the following statements is/are correct?
(a) Alcoholic group is tested by CAN test.
(b) Accurate method to determine the molecular weight of organic compound is 'cryoscopic method'.
(c) If there is 54% silver in a silver salt of a dibasic acid, then its (dibasic acid) molar mass is 186 g mol^{-1}.
(d) Diazonium salts form azo dyes with alkaline compounds.

SECTION 3 (Maximum Marks : 12)

- *This section contains TWO paragraphs.*
- *Based on each paragraph, there are TWO questions.*
- *Each question has Four options (a), (b), (c) and (d). ONLY ONE of these four options is correct.*
- *For each question, darken the bubble corresponding to the correct option in the ORS.*
- *For each question, marks will be awarded in one of the following categories :*

Full Marks : +3 *If only the bubble corresponding to the correct option is darkened.*

Zero Marks : 0 *In all other cases.*

Paragraph 1

Tollens' test is given by aldehydes.

$$Ag^+ + e^- \longrightarrow Ag; \qquad E^\circ_{red} = +0.800\text{ V}$$

$$C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7 + 2H^+ + 2e^- \qquad E^\circ_{ox} = -0.05\text{ V}$$

$$[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2NH_3 \qquad E^\circ_{red} = +0.373\text{ V}$$

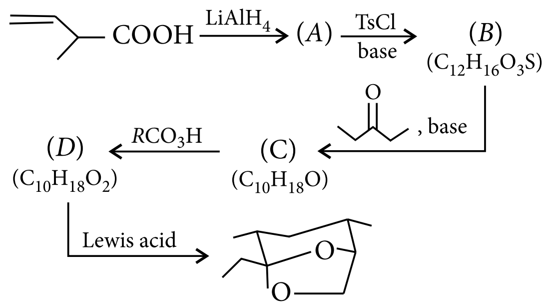
use $\left(\frac{F}{RT}\right) = 38.9\ V^{-1}$

15. Calculate ($\ln K$) for,
$$C_6H_{12}O_6 + 2Ag^+ + H_2O \longrightarrow C_6H_{12}O_7 + 2H^+ + 2Ag$$
(a) 55.6 (b) 29.6
(c) 66 (d) 58.35

16. NH_3 is used in this reaction rather than any other base. What is the correct reason for this?
(a) $[Ag(NH_3)_2]^+$ is a weaker oxidising agent than Ag^+.
(b) NH_3 prevents the decomposition of gluconic acid.
(c) Ag precipitates gluconic acid as its silver salt.
(d) NH_3 changes the standard reduction potential of $[Ag(NH_3)_2]^+$.

Paragraph 2

Shown below is a synthesis of elm bark beetle pheromone, multistriatin.

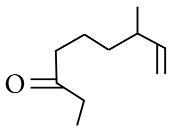
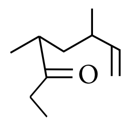
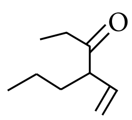
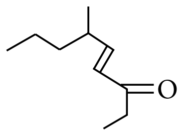


multistriatin

Based on the above synthesis, answer the following questions :

17. Tosylation is done in conversion of A to B in order to
(a) easily remove the –OH group of A
(b) reduce the –OH group
(c) oxidise the –OH group
(d) condense alcohols.

18. Structural formula of (C) is

(a) 
(b) 
(c) 
(d) 

SOLUTIONS

PAPER - I

1. **(a,c) :** (i) $Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2\uparrow$

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{\text{(Green)}}{Cr_2(SO_4)_3} + H_2O$

(ii) $4NO_2^- + 2H_2SO_4 \longrightarrow 4NO_2\uparrow + O_2\uparrow + SO_4^{2-} + 2H_2O$

As it does not produce orange red spots on starch paper, it cannot be Br_2. So, the anion is NO_3^-.

(iii) $SO_3^{2-} + Ba^{2+} \longrightarrow BaSO_3\downarrow$ (white)

$SO_3^{2-} + 2H^+ \longrightarrow SO_2\uparrow + H_2O$

(iv) $2NO_3^- + 4H_2SO_4 + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2NO\uparrow + 4SO_4^{2-} + 4H_2O$

$Fe^{2+} + 5H_2O + NO \longrightarrow [Fe(H_2O)_5NO]^{2+}$

2. **(a, b, c) :** (a) $\Delta_r H = 15 - 57.3 = -42.3$ kJ/mol

(b) $HA_{(g)} + BOH_{(g)} \xrightarrow{\Delta_r H} BA_{(aq)} + H_2O$

$HA_{(g)} \xrightarrow{-70.7\ \text{kJ}} HA_{(aq)}$; $BOH_{(g)} \xrightarrow{20\ \text{kJ}} BOH_{(aq)}$; $HA_{(aq)} + BOH_{(aq)} \xrightarrow{-42.3\ \text{kJ}} BA_{(aq)} + H_2O$

$\Delta_r H = -70.7 + 20 - 42.3 = -93$ kJ/mol

(c) $HA_{(g)} \xrightarrow{\Delta_r H} H^+_{(aq)} + A^-_{(aq)}$

$HA_{(g)} \xrightarrow{-70.7} HA_{(aq)} \xrightarrow{15} H^+_{(aq)} + A^-_{(aq)}$

$\Delta_r H = -70.7 + 15 = -55.7$ kJ/mol

(d) $BOH_{(g)} \longrightarrow BOH_{(aq)}$; $\Delta H = 20$ kJ/mol

$BOH_{(aq)} \longrightarrow B^+_{(aq)} + OH^-_{(aq)}$; $\Delta H = -57.3$ kJ/mol

Total $\Delta_r H = 20 - 57.3 = -37.3$ kJ/mol

3. **(a, d) :** Glucose $\xrightarrow{\text{anhydride, pyridine}}$ Pentaacetate derivative

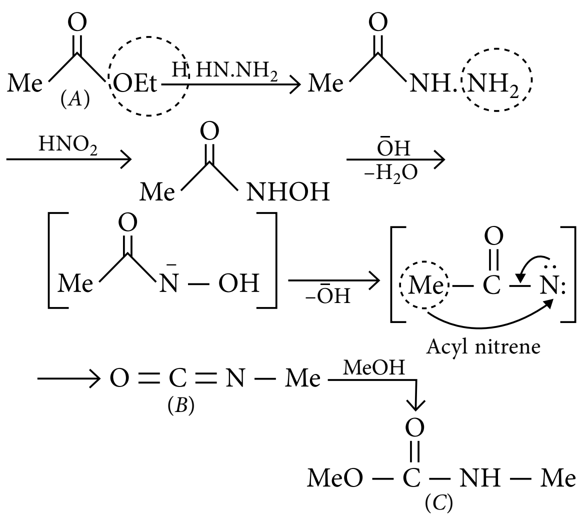
Glucose $\xrightarrow{NH_2OH}$ Form oxime

Pentaacetate derivative $\xrightarrow{NH_2OH}$ No reaction

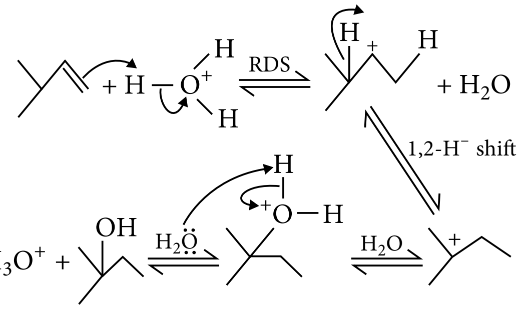
Confirms cyclic structure

Glycoside is functionally acetal which is formed from hemiacetal.

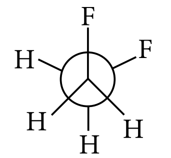
4. **(a,c) :** It is an example of Lossen rearrangement reaction.



5. **(a) :**

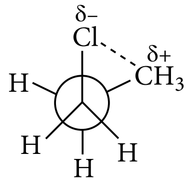


6. **(a,b,c,d):** $CH_2 - CH_2$ with F on each carbon



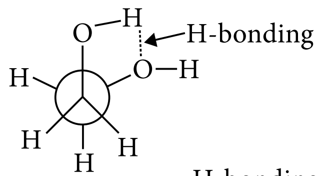
Delocalisation of bond-pair e^- of C–H bond in parallel ABMO of C–F is possible; leads to stability in gauche form

(b) $Cl - CH_2 - CH_2 - CH_3$

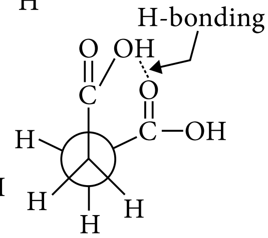


Due to +*I* nature of $-CH_3$, δ+ created on it while –*I* nature of –Cl induce δ– on it. Thus, dipole-dipole interaction leads to stability of gauche conformation.

(c) CH_2-CH_2 with OH on each carbon



(d) $HOOC - CH_2 - CH_2 - COOH$



7. **(a, b, c, d)**

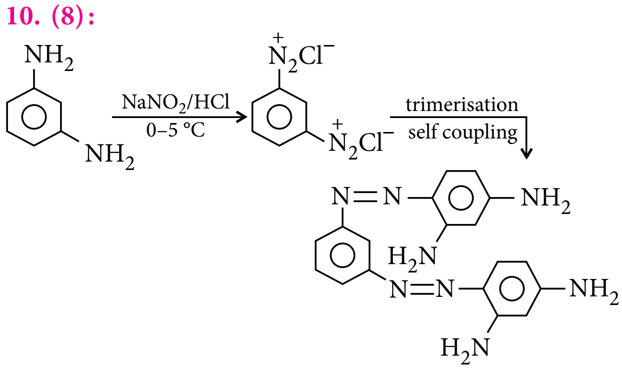
8. **(9):** $a = 3, b = 1, c = 5, d = 0 \Rightarrow (a + b + c + d) = 9$

9. **(3):** Fraction of edge unoccupied $(x) = \dfrac{a - 2r}{a}$

$$a = 2\sqrt{2}r,\ x = \frac{2(\sqrt{2}-1)}{2\sqrt{2}} = \frac{0.414}{1.414} = 0.293$$

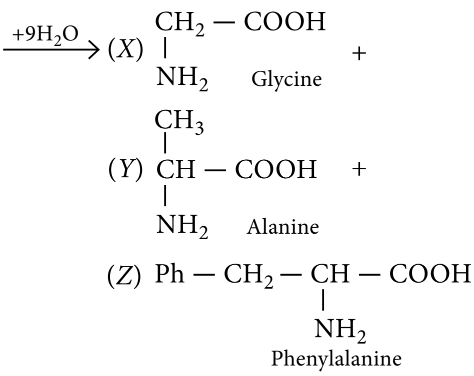
$$Z = \frac{x}{0.097} = \frac{0.293}{0.097} = 3$$

10. **(8):**



(Bismarck Brown)

11. (6): $\underbrace{\sim\text{Ⓖ}-CO-NH-\text{Ⓐ}-CO-NH-\text{Ⓟ}\sim}_{\text{Decapeptide}}$



Total wt. of amino acids after addition of 9 mole of $H_2O = 796 + 9 \times 18 = 958$

Since contribution of glycine is 47%.

$\therefore$ Total mass of glycine $= 958 \times 0.47 \approx 450$

Molar mass of glycine = 75

Therefore, no. of glycine molecules $= \dfrac{450}{75} = 6$

12. (8): $\%S_N1 = \dfrac{3\times10^{-6}[\text{substrate}]}{2.35\times10^{-5}[\text{subs.}]\times1.5 + 3\times10^{-6}[\text{subs.}]}\times100$

$= 7.824 \approx 8$

13. (c): $16\text{ g } NO_2 = \dfrac{16\text{ g}}{46\text{ g mol}^{-1}} = 0.35\text{ mol}$

1 mol represents 22.4 L at STP

So, 0.35 mol will be $= 22.4 \times 0.35$

$= 7.84\text{ L} = 7840\text{ mL}$

$\because$ 1 mol contains 6.023×10^{23} molecules

$\therefore$ 0.35 mol contains $6.023 \times 10^{23} \times 0.35$ molecules

$= 6.023 \times 10^{23} \times 0.35 \times 3$ atoms

$= 6.32 \times 10^{23}$ atoms

14. (b): $n = \dfrac{PV}{RT} = \dfrac{2.5\text{ atm}\times10.5\text{ L}}{0.0821\text{ L atm K}^{-1}\text{ mol}^{-1}\times300\text{ K}}$

$= 1.1$ mol

Volume of 1.1 mol $= 1.1 \times 22.4\text{ L} = 24.64\text{ L}$

$= 24640\text{ mL or } 24640\text{ cc}^3$

Number of molecules $= 1.1 \times 6.023 \times 10^{23}$

Number of atoms $= 1.1 \times 2 \times 6.023 \times 10^{23}$

$= 13.25 \times 10^{23}$

15. (b): 32 g sulphur $(S_8) = \dfrac{32\text{ g}}{32\times8\text{ g mol}^{-1}} = 0.125$ mol

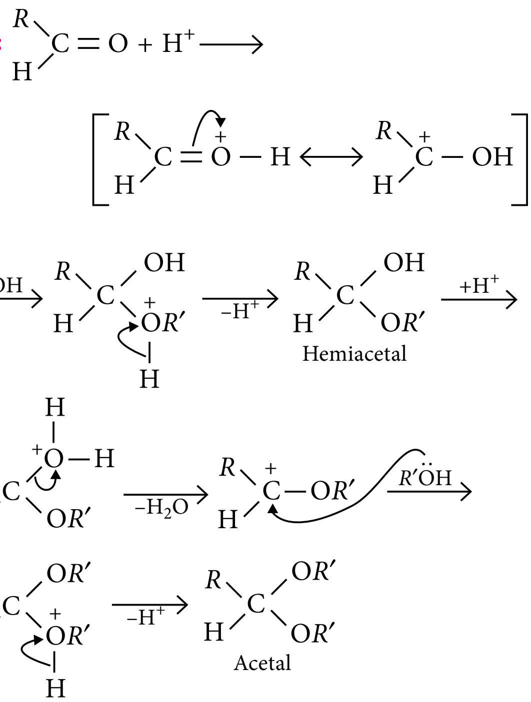
$0.125\text{ mol} \equiv 0.125 \times 22.4\text{ L} = 2.8\text{ L}$

0.125 mol contains $= 0.125 \times 6.023 \times 10^{23}$ molecules

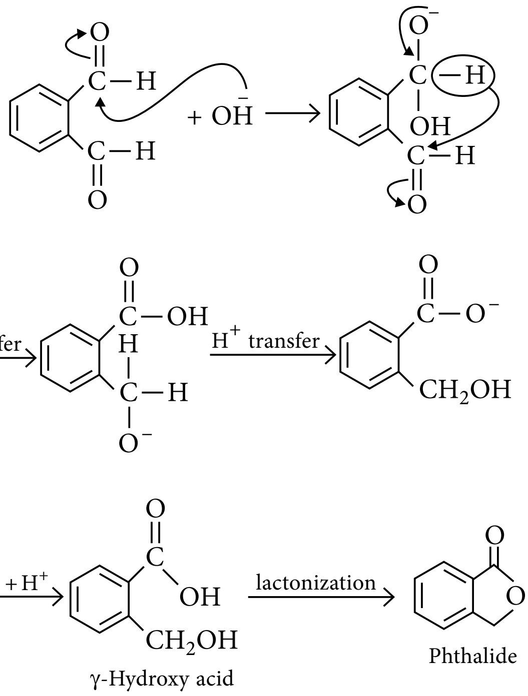
0.125 mol of S_8 contains $= 0.125 \times 6.023 \times 10^{23} \times 8$

$= 6.023 \times 10^{23}$ atoms

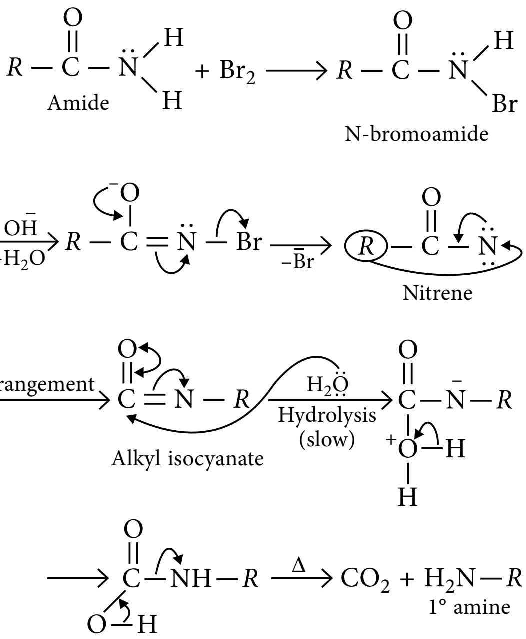
16. (b):



17. (c) :



18. (d):



PAPER - II

1. **(b):** At nodes, probability of finding of electron is zero.

$\therefore \quad \psi^2 = 0$ or $\psi = 0$

$\therefore \quad 6 - 6\sigma + \sigma^2 = 0; \sigma = 3 \pm \sqrt{3}$

For maximum distance $r = \dfrac{3}{2}\dfrac{(3+\sqrt{3})a_0}{Z}$

2. **(a):** $kt = \ln\dfrac{\alpha_0}{\alpha_t}$

$k \times 60 = \ln\dfrac{80}{75} \Rightarrow k = \dfrac{1}{60}\ln\dfrac{80}{75}$

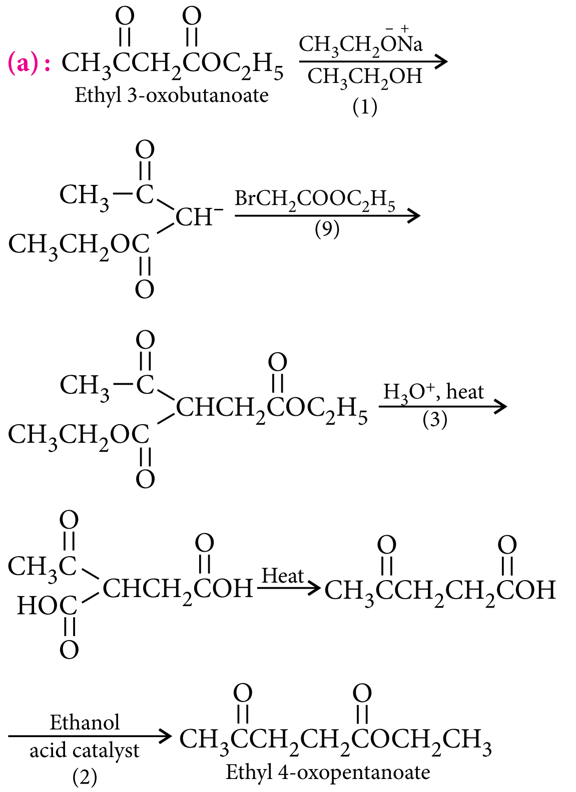
$k \times 5 \times 60 = \ln\dfrac{80}{r_t};\ 5\ln\dfrac{80}{75} = \ln\dfrac{80}{r_t};\ \ln\dfrac{80}{r_t} = 0.32$

$r_t = 58$

Optical rotation observed after 5 hrs = 58 + 2 = 60

3. **(b):** In isochoric process, volume is constant.

4. **(a):**



5. **(a):** Volume of unit cell $= (5 \times 10^{-8})^3$ cc
$= 1.25 \times 10^{-22}$ cc

Density of FeO = 4g/cc

Mass of unit cell $= 1.25 \times 10^{-22} \times 4 = 5 \times 10^{-22}$ g

Mass of 1 molecule $= \dfrac{72}{6.022 \times 10^{23}} = 1.195 \times 10^{-22}$ g

Hence, number of FeO molecules per unit cell

$$= \frac{5 \times 10^{-22}}{1.195 \times 10^{-22}} = 4.18 \approx 4$$

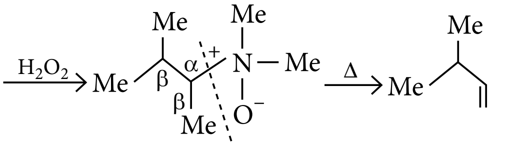
Hence, there are four Fe^{2+} and four O^{2-} ions in each unit cell.

6. **(a):** The bond angle 180° means *sp*-hybridisation which has 50% *s*-character.

7. **(d):** Complimentary DNA sequence : TTAGTCAA Complimentary RNA sequence : UUAGUCAA in DNA bases are bonded in complementary pair as A$=$T and G$\equiv$C while in RNA as A$=$U and G$\equiv$C.

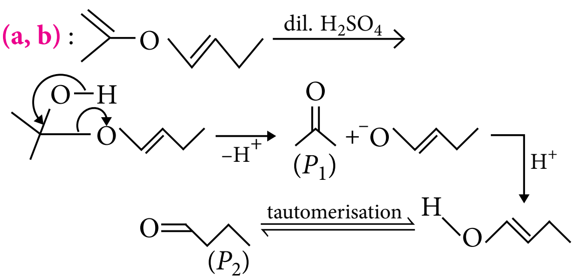
8. **(b,d) :** Amylase hydrolyses α-linkage. It exhibits mutarotation, since in β-*D*-glucose C-1 (OH) group is hemiacetalic.

9. **(a, c) :**
(a) The oxidation of 3° amine to amine oxide followed by Cope reaction on heating gives Hoffmann alkene (less substituted).

(a) 

(b) will not give Hoffmann alkene. Benzylic H atom is more acidic due to (–*I*) effect of Ph.
(c) will give Hoffmann alkene $CH_2=CH_2$.
(d) will not give Hoffmann alkene (Cope reaction).

10. **(a, b, c)**

11. **(a, b) :** 

12. **(b, c, d) :** In acidic medium, $KMnO_4$ gives 5 oxygen while acidic $K_2Cr_2O_7$ gives 3 oxygen and secondary alcohols are oxidised to ketones.
Tertiary alcohols are resistance to oxidation in neutral or alkaline $KMnO_4$ solution but are readily oxidised in acidic solution ($KMnO_4/H_2SO_4$) to a mixture of a ketone and an acid each contains lesser number of carbon atoms than the original alcohol.

13. **(a, c, d) :** Complex ions in which ligands can be interchanged rapidly are said to be labile.

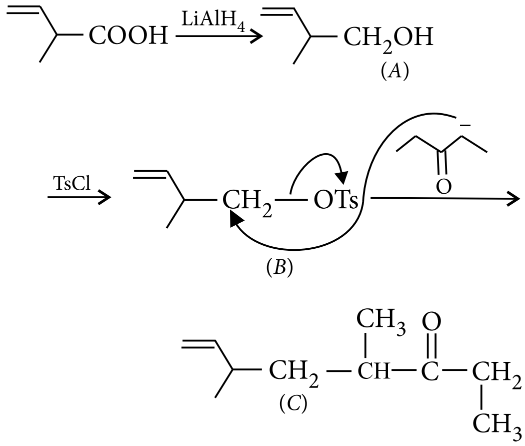
14. **(a, b c, d)**

15. **(d) :** $E^\circ_{cell} = E^\circ_R - E^\circ_L = 0.8 - 0.05 = 0.75$ V
$\Delta G^\circ_{cell} = -2FE^\circ_{cell} = -RT\ln K$

$$\ln K = \frac{2F}{RT} \times 0.75 = 2 \times 38.9 \times 0.75 = 58.35$$

16. **(a) :** Because $E^\circ_{Ag^+|Ag} > E^\circ_{[Ag(NH_3)_2]^+|Ag}$

17. **(a) :** – OTs is a good leaving group *i.e.* better than –OH group.

18. **(b) :** 

PRACTICE PAPER

AIIMS

Exam on 27th May 2018

1. Which of the following statements is incorrect?
   (a) The trivial names of organic compounds are called common names.
   (b) The systematic names of organic compounds are obtained from the IUPAC system.
   (c) The systematic names of alkanes are based on the number of C atoms in the longest continuous chain of C atoms.
   (d) The IUPAC name of $(CH_3)_2CHCH(CH_3)_2$ is 1,3-dimethylhexane.

2. If a compound, on analysis was found to contain C = 18.5%, H = 1.55%, Cl = 55.04% and O = 24.81%, then its empirical formula is
   (a) C_2H_2OCl (b) CH_2ClO_2
   (c) CHClO (d) $ClCH_2O$

3. Identify x, y and z for the following metallurgical process :
   $$\text{Metal sulphide} \xrightarrow{x} \text{Metal oxide} \xrightarrow{y} \text{Impure metal} \xrightarrow{z} \text{Pure metal.}$$
   x, y and z are respectively
   (a) roasting, smelting, electrolysis
   (b) roasting, calcination, smelting
   (c) calcination, auto-reduction, bassemerisation
   (d) none of the above is correct.

4. Ca^{2+} and F^- ions are located in CaF_2 crystal respectively at face centred cubic lattice points and in
   (a) tetrahedral voids
   (b) half of tetrahedral voids
   (c) octahedral voids
   (d) half of octahedral voids.

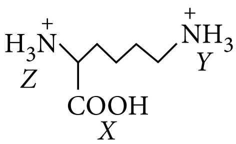
5. Which one of the following statements regarding photochemical smog is not correct?
   (a) Photochemical smog is formed by the combination of smoke, dust and fog containing sulphur dioxide from polluted air.
   (b) Photochemical smog causes irritation in eyes and throat.
   (c) Carbon monoxide does not play any role in photochemical smog formation.
   (d) Photochemical smog is oxidising in nature.

6. In ice, oxygen atom is surrounded
   (a) tetrahedrally by 4 hydrogen atoms
   (b) octahedrally by 2 oxygen and 4 hydrogen atoms
   (c) tetrahedrally by 2 hydrogen and 2 oxygen atoms
   (d) octahedrally by 6 hydrogen atoms.

7. Freshly obtained SnO_2 is added to water containing a little HCl. The sol obtained would be ______ due to preferential adsorption of ______ ions.
   (a) positively charged, H^+
   (b) negatively charged, SnO_3^{2-}
   (c) positively charged, Sn^{4+}
   (d) positively charged, Sn^{2+}

8. Non-stick cookwares generally have a coating of a polymer, whose monomer is
   (a) $CH_2=CH_2$ (b) $CH_2=CHCN$
   (c) $CH_2=CHCl$ (d) $CF_2=CF_2$

9. The correct order of electron gain enthalpy values ($\Delta_{eg}H$) of the halogen atoms is
   (a) F < Cl < Br < I (b) I < Br < F < Cl
   (c) I < Br < Cl < F (d) Cl < Br < I < F

10. 
   Arrange X, Y and Z in order of decreasing acidic strength.
   (a) $X > Z > Y$ (b) $Z < X < Y$
   (c) $X > Y > Z$ (d) $Z > X > Y$

11. If $K_{sp(\text{AgCNS})} = 1 \times 10^{-12}$ and $K_{sp(\text{AgBr})} = 5 \times 10^{-13}$, then the values of simultaneous solubility of AgCNS and AgBr in a solution of water will be

(a) 8.16×10^{-7}, 4.08×10^{-7}
(b) 4.08×10^{-7}, 8.16×10^{-7}
(c) 8.16, 4.08
(d) 1×10^{-12}, 5×10^{-13}

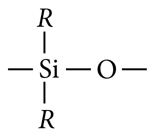
12. Arrange the following compounds in order of increasing dipole moment :

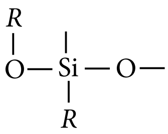
I. Toluene II. *m*-Dichlorobenzene
III. *o*-Dichlorobenzene IV. *p*-Dichlorobenzene

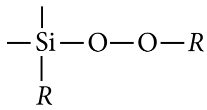
(a) I < IV < II < III (b) IV < I < II < III
(c) IV < I < III < II (d) IV < II < III < I

13. The repeating unit in silicone is

(a) SiO_2

(b) 

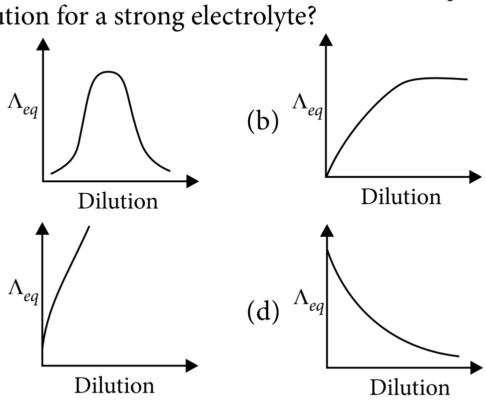
(c) 

(d) 

14. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$, the major product is monobromonitrobenzene. Which of the following statements is related to the process?

(a) Electron density on *meta*-carbon is more than that on *ortho*- or *para*-carbons.
(b) Loss of aromaticity occurs, when Br^+ attacks at the *ortho*- or *para*-positions and not at *meta*-position.
(c) Intermediate carbocation formed after initial attack of Br^+ at the *meta*-position is least stabilised.
(d) Easier loss of H^+ from *meta*-position than from *ortho*- and *para* -position to regain aromaticity.

15. Which of the following plots correctly represents variation of equivalent conductance (Λ_{eq}) with dilution for a strong electrolyte?



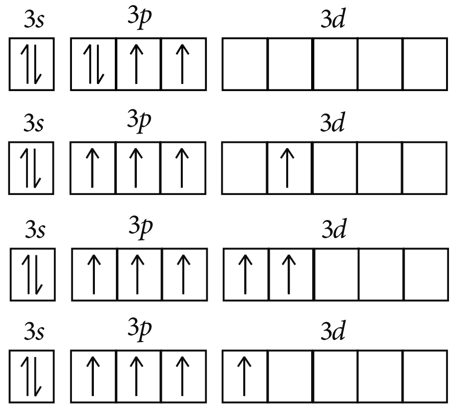
16. Which of the following does not represent the mathematical expression for the Heisenberg uncertainty principle?

(a) $\Delta x.\Delta p \geq \dfrac{h}{4\pi}$ (b) $\Delta x.\Delta v \geq \dfrac{h}{4\pi m}$

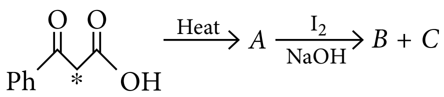
(c) $\Delta E.\Delta t \geq \dfrac{h}{4\pi}$ (d) $\Delta E.\Delta x \geq \dfrac{h}{4\pi}$

17. Which of the following has maximum energy?

(a)
(b)
(c)
(d)

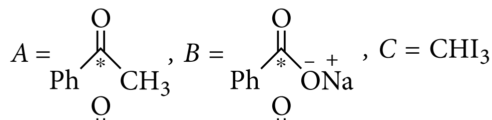


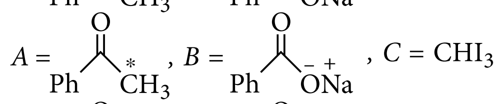
18. In the following reactions sequence,

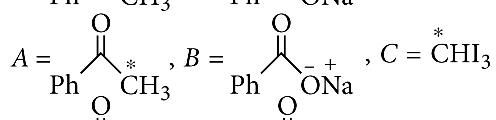


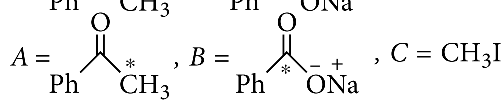
(* implies ^{13}C labelled carbon)

the correct structures of *A*, *B* and *C* are

(a) 

(b) 

(c) 

(d) 

19. Extraction of zinc from zinc blende is achieved by

(a) electrolytic reduction
(b) roasting followed by reduction with carbon
(c) roasting followed by reduction with another metal
(d) roasting followed by self-reduction.

20. The pair of amphoteric hydroxides is

(a) $Al(OH)_3$, LiOH
(b) $Be(OH)_2$, $Mg(OH)_2$
(c) $B(OH)_3$, $Be(OH)_2$
(d) $Be(OH)_2$, $Zn(OH)_2$.

21. A solution containing 2.675 g of $CoCl_3.6NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.75 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is
(a) $[CoCl_3(NH_3)_3]$ (b) $[CoCl(NH_3)_5]Cl_2$
(c) $[Co(NH_3)_6]Cl_3$ (d) $[CoCl_2(NH_3)_4]Cl$

22. To prepare a solution of concentration of 0.03 g/mL of $AgNO_3$, what amount of $AgNO_3$ should be added in 60 mL of solution?
(a) 1.8 g (b) 0.8 g
(c) 0.18 g (d) None of these

23. A solution is 0.1 M with respect to Ag^+, Ca^{2+}, Mg^{2+} and Al^{3+}. Which will precipitate at lowest concentration of PO_4^{3-} ion when Na_3PO_4 solution is added?
(a) $Ag_3PO_4(K_{sp} = 1 \times 10^{-6})$
(b) $Ca_3(PO_4)_2$ $(K_{sp} = 1 \times 10^{-33})$
(c) $Mg_3(PO_4)_2(K_{sp} = 1 \times 10^{-24})$
(d) $AlPO_4(K_{sp} = 1 \times 10^{-20})$

24. Which of the following is the correct representation of relative lowering of vapour pressure?
(a) $\frac{P^o}{\Delta P} = \frac{P^o - P}{P^o}$ (b) $\frac{\Delta P}{P^o} = \frac{P - P^o}{P^o}$
(c) $\frac{P^o}{\Delta P} = \frac{P^o}{P^o - P}$ (d) $\frac{\Delta P}{P^o} = \frac{P^o - P}{P^o}$

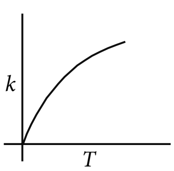
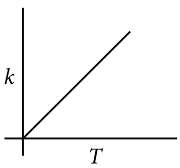
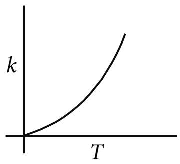
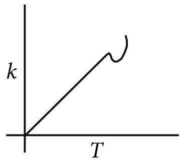
25. The reaction of cyanamide (NH_2CN) with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be –742.7 kJ mol^{-1} at 298 K. Calculate the enthalpy change for the reaction at 298 K.

$$NH_2CN_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$$

(a) –741.46 kJ mol^{-1} (b) –743.9 kJ mol^{-1}
(c) +741.46 kJ mol^{-1} (d) +743.9 kJ mol^{-1}

26. Among the following which is least acidic?
(a) Phenol (b) *o*-Cresol
(c) *p*-Nitrophenol (d) *p*-Chlorophenol

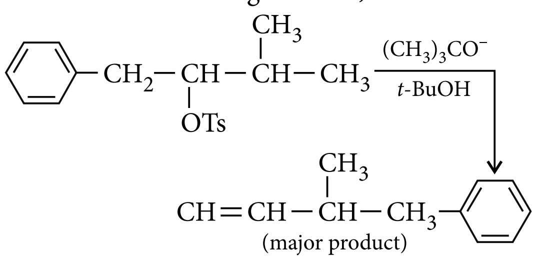
27. Which curve corresponds to the temperature dependance of the rate constant (k) of a simple one step reaction?

(a) 
(b) 
(c) 
(d) 

28. It is desired to increase the volume of 80 cm^3 of a gas by 20% without changing pressure. To what temperature the gas should be heated if its initial temperature is 25 °C?
(a) 35.6 °C (b) 84.6 °C
(c) 630.6 °C (d) 35 °C

29. $CCl_3CH{=}CH_2 \xrightarrow{Cl_2 + H_2O} A$; A is
(a) $CCl_3CH(OH)CH_2Cl$ (b) $CCl_3CH(Cl)CH_2OH$
(c) $CCl_3CH(Cl)CH_2Cl$ (d) $CCl_3CH(OH)CH_2OH$

30. Consider the following reaction,



The correct explanation is
(a) the product is formed due to nucleophilic substitution
(b) the product is formed according to Saytzeff's rule
(c) conjugated double bond product is formed due to higher stability by resonance
(d) $(CH_3)_3CO^-$ is a better leaving group.

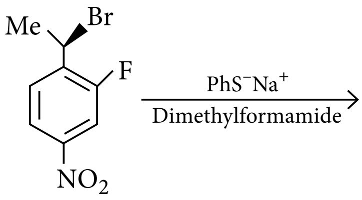
31. Which of the following cannot be made by using Williamson's synthesis?
(a) Di-*tert*-butyl ether (b) Methoxybenzene
(c) Benzyl *p*-nitrophenyl ether
(d) Methyl *tert*-butyl ether

32. Metal carbide on reaction with water forms CH_4. Carbide can be
(a) CaC_2 (b) Mg_3C_2 (c) Be_2C (d) SiC

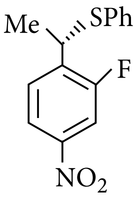
33. Time required to deposit one millimole of aluminium metal by the passage of 9.65 amperes through aqueous solution of aluminium ion is
(a) 30 s (b) 10 s
(c) 30,000 s (d) 10,000 s.

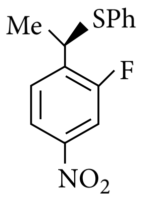
34. The correct order of dipole moment is
(a) $CH_4 < NF_3 < NH_3 < H_2O$
(b) $NF_3 < CH_4 < NH_3 < H_2O$
(c) $NH_3 < NF_3 < CH_4 < H_2O$
(d) $H_2O < NH_3 < NF_3 < CH_4$

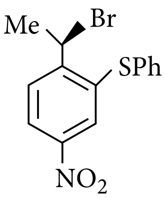
35. The major product of the following reaction,

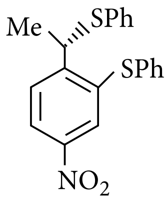


is

(a) 

(b) 

(c) 

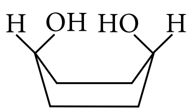
(d) 

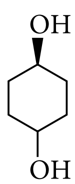
36. Which of the following electrolytes will have maximum flocculation value for $Fe(OH)_3$ sol?
(a) NaCl (b) Na_2S
(c) $(NH_4)_3PO_4$ (d) K_2SO_4

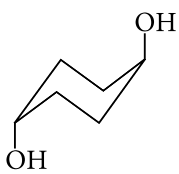
37. Which of the following fluorides has the lowest melting point?
(a) BaF_2 (b) SrF_2 (c) CaF_2 (d) BeF_2

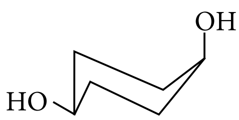
38. Which of the following pairs have both the elements showing highest oxidation states equal to $[ns + (n - 1)d]$ electrons
(a) Ti and Fe (b) Cr and Co
(c) Cr and Mn (d) Co and Ni.

39. Which form of *trans*-1, 4-cyclohexanediol is most stable?

(a) 

(b) 

(c) 

(d) 

40. A gas z is bubbled through a solution containing x^- and y^- ions. If the reduction potential are in the order $x > y > z$, then
(a) y will oxidise z and not x
(b) y will oxidise x and not z
(c) y will oxidise both x and z
(d) y will reduce both x and z.

ASSERTION AND REASON

Directions : In the following questions (41-60), a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

41. **Assertion :** Photochemical smog is produced by nitrogen oxides.
Reason : Vehicular pollution is a major source of nitrogen oxides.

42. **Assertion :** The reaction,
$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ is favoured in the forward direction with increase of pressure.
Reason : The reaction is exothermic.

43. **Assertion :** A catalyst enhances the rate of a reaction.
Reason : A catalyst remains unchanged in mass and in chemical composition at the end of the reaction.

44. **Assertion :** The micelle formed by sodium stearate in water has $-COO^-$ groups at the surface.
Reason : Surface tension of water is reduced by the addition of stearate.

45. **Assertion :** Kinetic gas equation is modified for real gases.
Reason : This modification is carried out with respect to actual volume of molecules and attractive forces between the gaseous molecules.

46. **Assertion :** The total number of stereoisomers shown by $[Co(en)_2Cl_2]^+$ complex ion is three.
Reason : $[Co(en)_2Cl_2]^+$ complex ion has octahedral geometry.

47. **Assertion:** 0.1 M aqueous solution of glucose has same depression in the freezing point as 0.1 M aqueous solution of urea.
Reason: K_f value for both the solutions is same.

48. **Assertion :** Diamond and graphite do not have the same crystal structures.
Reason : Diamond is crystalline while graphite is amorphous.

49. Assertion : Helium has the highest value of ionisation energy among all the elements known.
Reason : Helium has the highest value of electron affinity among all the elements known.

50. Assertion : In H_2SO_5, oxidation number of S is +6.
Reason : There is one peroxide linkage in H_2SO_5.

51. Assertion : Absorption spectrum consists of some bright lines separated by dark spaces.
Reason : Emission spectrum consists of dark lines.

52. Assertion : S_N2 reaction of an optically active alkyl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.
Reason : S_N2 reactions proceed with inversion of configuration.

53. Assertion : Benzene on heating with conc. H_2SO_4 gives benzenesulphonic acid which when heated with superheated steam under pressure gives benzene.
Reason : Sulphonation is a reversible process.

54. Assertion : Sucrose is a non-reducing sugar.
Reason : It has glycosidic linkage.

55. Assertion : Calgon is not suitable for removing Ca^{2+} and Mg^{2+} ions from hard water.
Reason : Calgon forms insoluble complex with Ca^{2+} and Mg^{2+} ions.

56. Assertion : Anilinium chloride is more acidic than ammonium chloride.
Reason : Anilinium ion is resonance stabilized.

57. Assertion : Essential oils are purified by steam distillation.
Reason : Essential oils are insoluble in water and are non-volatile in steam.

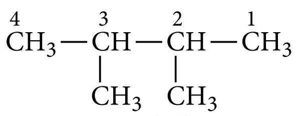
58. Assertion : Aqueous solution of $CoCl_2$ is pink in colour. It turns blue in presence of conc. HCl.
Reason : It is due to the formation of $[CoCl_4]^{2-}$.

59. Assertion : Mercury is liquid at room temperature.
Reason : In mercury, there is no unpaired *d*-electron and thus metallic bonding is weakest.

60. Assertion : The bond order of helium is always zero.
Reason : The number of electrons in bonding molecular orbital and antibonding molecular orbital is equal.

SOLUTIONS

1. (d) :



2, 3-Dimethylbutane

2. (c) :

Element	%	Atomic mass	Relative number of atoms	Simplest ratio of atoms
C	18.5	12	$\frac{18.5}{12} = 1.542$	1
H	1.55	1	$\frac{1.55}{1} = 1.55$	1
Cl	55.04	35.5	$\frac{55.04}{35.5} = 1.55$	1
O	24.81	16	$\frac{24.81}{16} = 1.55$	1

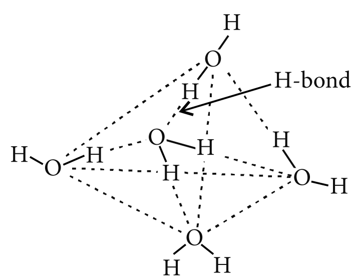
Therefore, empirical formula of the compound is CHClO.

3. (a) : The conversion of metal sulphide to metal oxide involves the process of roasting *i.e.*, *x* is roasting. The metal oxides can then be converted to impure metal by reduction *i.e.*, '*y*' is smelting.
The conversion of impure metal to pure metal involves a process of purification. Thus, '*z*' is electrolysis.

4. (a) : In CaF_2 crystal, Ca^{2+} ions are present at corners and at the centre of each face of the cube while F^- ions occupy all the tetrahedral voids.

5. (a) : Classical smog is formed by the combination of smoke, dust and fog containing sulphur dioxide from polluted air.

6. (a) : X-ray studies have shown that in ice, four hydrogen atoms tetrahedrally surround each oxygen atom.



Tetrahedral arrangement of water

7. (c) : $SnO_2 + 4HCl \longrightarrow Sn^{4+} + 4Cl^- + 2H_2O$
Sn^{4+} ions are preferentially adsorbed by SnO_2 particles.

8. (d) : $nCF_2{=}CF_2 \longrightarrow \underset{\text{Teflon}}{+\!\!\!\!\left[CF_2{-}CF_2\right]_n}$

Teflon is used for non-stick cookwares.

9. (b) : As we move from Cl to I, the electron gain enthalpy becomes less and less negative due to increase in the atomic radius. Due to small size of F, the electron-electron repulsions in the relatively compact 2p-subshell are comparatively large and hence, the incoming electron is not accepted with the same ease as in case of Cl. Consequently, the electron gain enthalpy of F is less negative than that of Cl.

10. (a) : Carboxylic acid is stronger acid than $\overset{+}{N}H_3$, therefore, X is the strongest acid. Since, —COOH has $-I$-effect which decreases with distance, therefore, $-I$-effect is more pronounced on Z than on Y. As a result, Z is more acidic than Y. Thus, overall order of decreasing acidic strength is $X > Z > Y$.

11. (a) : $AgCNS \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{CNS^-}$

$$AgBr \rightleftharpoons \underset{y}{Ag^+} + \underset{y}{Br^-}$$

$\therefore \quad [Ag^+] = (x + y), [CNS^-] = x, [Br^-] = y$

$K_{sp[AgCNS]} = [Ag^+]\,[CNS^-] = x\,(x + y)$

$\Rightarrow \quad 1 \times 10^{-12} = x(x + y)$ ...(i)

and, $K_{sp[AgBr]} = [Ag^+]\,[Br^-] = y(x + y)$

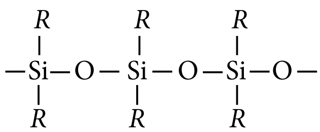
$\Rightarrow \quad 5 \times 10^{-13} = y(x + y)$ ...(ii)

On solving eqn (i) and (ii), we get

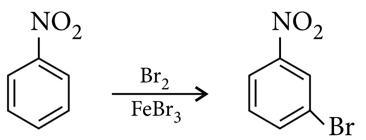
$x = 8.16 \times 10^{-7}$ mol/L, $y = 4.08 \times 10^{-7}$ mol/L

12. (b) : Dipole moment of p-dichlorobenzene is zero whereas o- and m-dichlorobenzene have higher dipole moment than toluene. Again o-dichlorobenzene has higher dipole moment than m-dichlorobenzene. Hence, the order is IV < I < II < III.

13. (b) : R_2SiO— is the repeating unit in silicone.

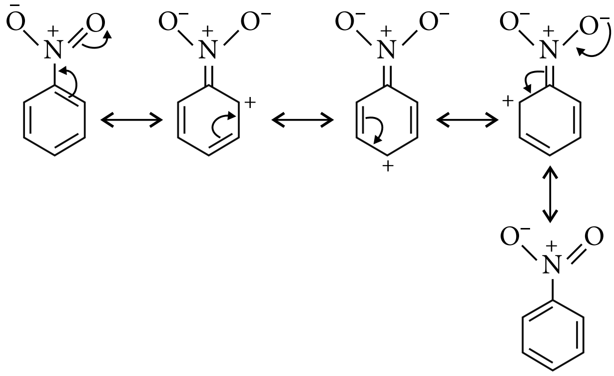


14. (a) :



Nitrobenzene — m-Bromonitrobenzene

This reaction is aromatic electrophilic substitution reaction. $-NO_2$ group being a powerful electron withdrawing group deactivates the benzene ring and provides the electron density at $meta$-position which can be shown by resonating structures.



Hence, reaction occurs at $meta$-position not at $ortho$- or $para$-position.

15. (b) : Equivalent conductance increases with dilution and ultimately becomes constant.

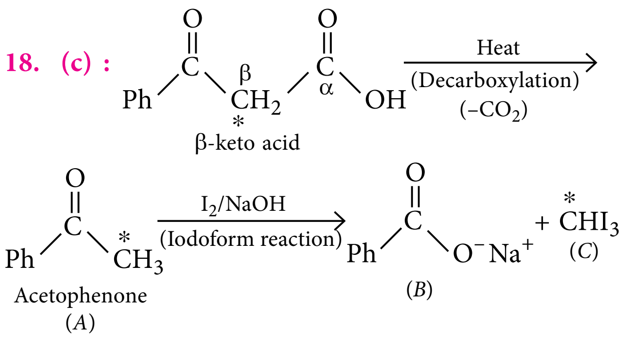
16. (d) : Heisenberg uncertainty principle can be written as,

$$\Delta x.\Delta p \geq \frac{h}{4\pi} \text{ or } \Delta x.m\Delta v \geq \frac{h}{4\pi} \Rightarrow \Delta x.\Delta v \geq \frac{h}{4\pi m}$$

Also, $\Delta p.\Delta x = \Delta E.\Delta t \Rightarrow \Delta E.\Delta t \geq \dfrac{h}{4\pi}$

17. (c) : The order of increasing energy of the subatomic orbitals is $s < p < d < f$. The energy in excited state is more than that in the ground state. Since option (c) is an excited state with maximum number of unpaired electrons, therefore it has maximum energy.

18. (c) :



19. (b)

20. (d) : Both $Be(OH)_2$ and $Zn(OH)_2$ are amphoteric in nature.

21. (c) : Moles of the complex $= \dfrac{2.675}{267.5} = 0.01$

Moles of AgCl precipitated $= \dfrac{4.75}{143.5} = 0.033$

Thus, 1 mole of the complex will precipitate

$= \dfrac{0.033}{0.01} = 3$ moles of AgCl

This means that 1 molecule of the complex contains 3 ionisable Cl. Hence, the formula is $[Co(NH_3)_6]Cl_3$.

22. (a) : Concentration in terms of g/mL is given as

$$0.03 = \frac{\text{mass of } AgNO_3}{60}$$

Mass of $AgNO_3 = 60 \times 0.03 = 1.8$ g

23. (d) : (a) $Ag_3PO_4 \rightleftharpoons 3Ag^+ + \underset{0.1}{PO_4^{3-}}$

$K_{sp} = [Ag^+]^3[PO_4^{3-}]$

$$[PO_4^{3-}] = \frac{K_{sp}}{(0.1)^3} = \frac{1\times10^{-6}}{10^{-3}} = 10^{-3}\,\text{M}$$

(b) $Ca_3(PO_4)_2 \rightleftharpoons \underset{0.1}{3Ca^{2+}} + 2PO_4^{3-}$

$K_{sp} = [Ca^{2+}]^3\,[PO_4^{3-}]^2$

$10^{-33} = (0.1)^3\,[PO_4^{3-}]^2$

$$[PO_4^{3-}]^2 = \frac{10^{-33}}{10^{-3}} = 10^{-30}$$

$[PO_4^{3-}] = 10^{-15}$ M

(c) $Mg_3(PO_4)_2 \rightleftharpoons \underset{0.1}{3Mg^{2+}} + 2PO_4^{3-}$

$$[PO_4^{3-}]^2 = \frac{10^{-24}}{10^{-3}} = 10^{-21}$$

$[PO_4^{3-}] = 3.16 \times 10^{-11}$ M

(d) $AlPO_4 \rightleftharpoons \underset{0.1}{Al^{3+}} + PO_4^{3-}$

$$\left[PO_4^{3-}\right] = \frac{K_{sp}}{0.1} = \frac{10^{-20}}{0.1} = 10^{-19}\text{ M}$$

24. (d)

25. (a) : $NH_2CN_{(s)} + \frac{3}{2}O_{2(g)} \longrightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$

$$\Delta n_g = n_p - n_r = 2 - \frac{3}{2} = \frac{1}{2} = 0.5\text{ mol}$$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta H = -742.7\text{ kJ mol}^{-1} + (0.5\text{ mol} \times 8.314 \times 10^{-3}\text{ kJ mol}^{-1}\text{ K}^{-1} \times 298\text{ K})$

$\Delta H = (-742.7\text{ kJ} + 1238.786 \times 10^{-3}\text{ kJ})\text{ mol}^{-1}$
$= -741.46\text{ kJ mol}^{-1}$

26. (b) : When an electron withdrawing group (like $—NO_2$, —Cl) is attached to the phenol ring, it stabilises the negative charge on the oxygen of phenoxide ion. Due to this reason, acidic character of phenol increases. But when an electron donating group (like $—CH_3$) is attached to the phenol ring, it destabilises the ring and hence, acidic character of phenol decreases. Thus, the correct order of acidic character is
p-nitrophenol > *p*-chlorophenol > phenol > *o*-cresol.

27. (c) : Rate constant k increases exponentially as T increases.

$$k = Ae^{-E_a/RT} = \frac{A}{e^{E_a/RT}}$$

28. (b) : The desired increase in the volume of gas is

$$20\% \text{ of } 80\text{ cm}^3 = \frac{80}{100} \times 20 = 16\,\text{cm}^3$$

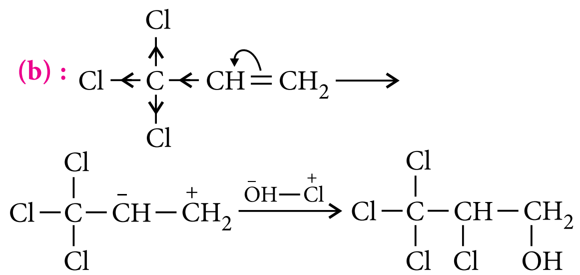
Thus, the final volume of the gas is 80 + 16 = 96 cm^3
Now, $V_1 = 80$ cm^3, $V_2 = 96$ cm^3
$T_1 = 25$ °C = 298 K, T_2 = ?
Applying Charles' law, we get

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$T_2 = \frac{V_2T_1}{V_1} = \frac{96\,\text{cm}^3 \times 298\text{ K}}{80\,\text{cm}^3} = 357.6\text{ K}$$

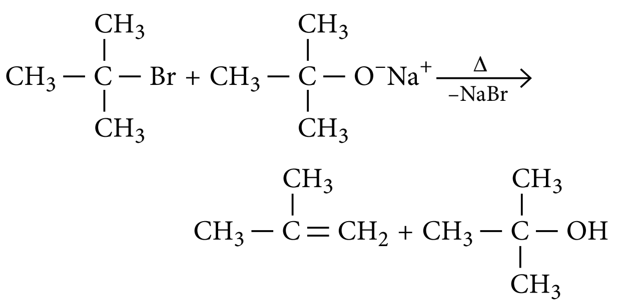
$= 357.6 - 273 = 84.6$ °C

29. (b) :



30. (c) : $(CH_3)_3CO^-$ is a better base than a nucleophile. Hence, elimination occurs. The product formed is resonance stabilised.

31. (a) : Di-*tert*-butyl ether cannot be made by Williamson's synthesis, since *tert*-alkyl halides prefer to undergo elimination rather than substitution, *i.e.*,



32. (c) : $Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$

33. (a) : $Al^{3+} + 3e^- \rightarrow Al$

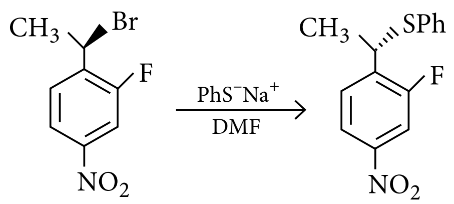
For deposition of 1 mole of Al^{3+}, charge required $\equiv 3 \times 96500$ C

For deposition of 1 millimole of Al^{3+}, charge required $\equiv 3 \times 96.500$ C

As $Q = It \Rightarrow t = \frac{Q}{I} = 3 \times \frac{96.5}{9.65} = 30$ s

34. (a) : In H_2O, electronegativity difference is highest. So, dipole moment is highest in H_2O. CH_4 has a symmetrical tetrahedral structure and its dipole moment is zero. Net dipole moment of NF_3 is less than that of NH_3.

35. (a) : This reaction will not proceed via S_N1 mechanism as the carbocation formed will be destabilised by the $-I$ effect of flourine and $-R$ effect of —NO_2 group. Benzyl halides are more reactive than aryl halides in S_N2 reactions. Therefore, the reaction occurs in the side chain with inversion of configuration at the chiral centre.



36. (a) : Flocculation value $\propto \frac{1}{\text{Coagulating power}}$

Greater the coagulating power of effective ion, lower will be the flocculation value of the electrolyte.

$Fe(OH)_3$ is a positively charged sol. According to Hardy Schulze rule, greater the charge on the oppositively charged ion of the electrolyte added, more effective it is in coagulation.

Among the four electrolytes, NaCl has the lowest coagulating power, so its flocculation value will be maximum.

37. (d) : Being covalent, BeF_2 has the lowest melting point (554°C) while other fluorides melt at around 1400°C.

38. (c) : Cr and Mn show the highest oxidation states +6 and +7 respectively.

39. (a) : When intramolecular hydrogen bonding is possible between groups at 1 and 4 positions the molecule assumes a boat conformation rather than the chair conformation in which hydrogen bonding is not possible.

40. (a) : More the value of reduction potential, more is the tendency to accept electrons or get reduced. As gas z has lowest reduction potential, therefore, z will be oxidised easily.

41. (b) : NO_2 + U.V. light $\rightarrow$ NO + O

Atomic oxygen produced as above reacts with hydrocarbons to give a variety of free hydrocarbon radicals, aldehydes, ketones, O_3, peroxyacetyl nitrate (PAN), etc. PAN mixes with the fog and gets condensed on smoke or dust particles in the air to form a smog which is called photochemical smog.

42. (b) : According to Le-Chatelier's principle, with increase of pressure, equilibrium shifts in that direction in which lesser number of moles of gaseous products are produced.

43. (b)

44. (b) : Micelle is formed if molecules with polar and non-polar ends assemble in bulk to give non-polar interior and polar exterior.

45. (a) : The kinetic gas equation for one mole of a real gas is $\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$

This is known as van der Waals' equation.

46. (b) : $[Co(en)_2Cl_2]^+$ exist in two geometrical isomers *cis* and *trans*. *Trans* isomer does not show optical isomerism since it is symmetrical while *cis*-isomer shows optical isomerism and exists as *d*- and *l*-form. So, total three stereoisomers are possible.

47. (b) : Depression in freezing point is a colligative property which depends on the number of particles present in the solution. As both 0.1 M solution of glucose and 0.1 M solution of urea contain same number of particles therefore, both will have same depression in freezing point.

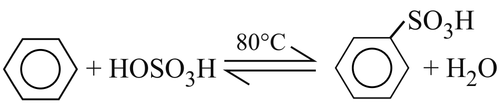
48. (c) : Diamond and graphite both are crystalline. Crystalline structure is different as in diamond, C-atoms are sp^3-hybridised while in graphite, they are sp^2-hybridised.

49. (c) : Helium contains fully filled $1s^2$ orbital which has more penetrating effect and is very close to the nucleus and hence, has higher value of ionisation energy. The electron affinity of He is the lowest of all the noble gases, due to the smallest size of He.

50. (a)

51. (d) : Absorption spectrum is produced when white light is passed through a substance and transmitted light is analysed by a spectrograph. The dark spaces corresponds to the light radiation absorbed by the substance. An emission spectrum is produced by analysing the radiant energy emitted by an excited substance by a spectrograph. Thus, discontinuous spectra consisting of a series of sharp lines and separated by dark bands are obtained.

52. (a)

53. (a) : 

54. (a) : Sucrose is a non-reducing sugar as it does not reduce Tollens' or Fehling's reagent, due to absence of free aldehyde or ketone group. It contains stable acetal or ketal structure which cannot be opened into a free carboxyl group.

Sugar is composed of α-*D*-glucopyranose unit and β-*D*-fructofuranose unit. These units are joined by α, β-glycosidic linkage between C-1 of the glucose unit and C-2 of the fructose unit.

55. (d) : Calgon is used to treat hard water by removing Ca^{2+} and Mg^{2+} ions in the form of soluble complexes.

56. (c) : Anilinium ion is not resonance stabilised since nitrogen does not have a lone pair of electrons.

57. (c) : Essential oils are insoluble in water and are volatile in steam.

58. (a) : $$\underset{\text{Pink}}{[Co(H_2O)_6]^{2+}_{(aq.)}} + 4Cl^-_{(aq)} \rightleftharpoons \underset{\text{Blue}}{[CoCl_4]^{2-}_{(aq.)}} + 6H_2O_{(l)}$$

According to Le Chatelier's principle, on adding conc. HCl, the equilibrium shifts in forward direction giving blue colour.

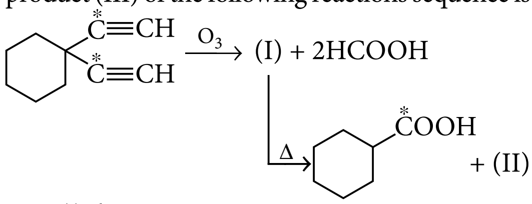
59. (a) **60. (a)**

GEAR UP FOR JEE MAIN

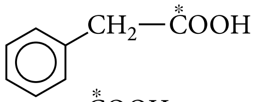
EXAM ON
8th April (Offline)
15th & 16th April (Online)
2018

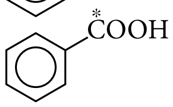
1. Which of the following thermodynamic conditions at constant pressure and temperature is necessary for the spontaneity of a process?
   (a) $d(U - TS + PV) > 0$
   (b) $d(U - TS + PV) < 0$
   (c) $d(U - TS + PV) = 0$
   (d) $d(U + TS + PV) < 0$

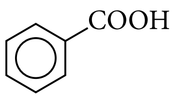
2. The product (III) of the following reactions sequence is

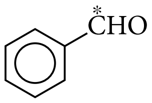
   (i) 

   (ii) $(II) \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) PhMgBr}} (III)$

   (a) 

   (b) 

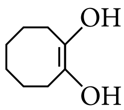
   (c) 

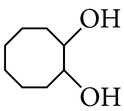
   (d) 

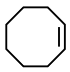
3. In the manufacture of H_2SO_4, the nitrated acid from the Gay-Lussac's tower is chemically
   (a) $NO_2{\cdot}H_2SO_4$
   (b) $NO{\cdot}H_2SO_4$
   (c) $NO{\cdot}2H_2SO_4$
   (d) $NO{\cdot}HSO_4$

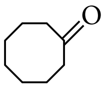
4. Find the equilibrium constant for the reaction,
   $Cu^{2+} + In^{2+} \rightleftharpoons Cu^+ + In^{3+}$
   Given that, $E^\circ_{Cu^{2+}|Cu^+} = 0.15$ V, $E^\circ_{In^{2+}|In^+} = -0.4$ V, $E^\circ_{In^{3+}|In^+} = -0.42$ V
   (a) 10^{10}
   (b) 10^{15}
   (c) 10^{20}
   (d) 10^{18}

5. The reaction of cyclooctyne with $HgSO_4$ in the presence of aqueous H_2SO_4 gives

   (a) 

   (b) 

   (c) 

   (d) 

6. For the two gaseous reactions, following data is given :
   $A \to B;\ k_1 = 10^{10}\, e^{-20000/T}$
   $C \to D;\ k_2 = 10^{12}\, e^{-24606/T}$
   the temperature at which k_1 becomes equal to k_2 is
   (a) 400 K
   (b) 1000 K
   (c) 800 K
   (d) 1500 K

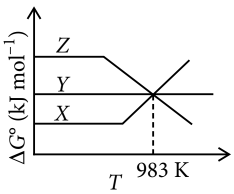
7. The number of hexagonal faces present in a truncated octahedron is
   (a) 6
   (b) 8
   (c) 4
   (d) 16

8. Identify the product for the given reaction.

   $$CH_3-CH_2-\overset{O}{\overset{||}{C}}-OC_2H_5 \xrightarrow[H_2O]{Na\overset{*}{O}H} \text{Product}$$

   (a) $CH_3-CH_2-\overset{O}{\overset{||}{C}}-\overset{*}{O}^-$
   (b) $CH_3-CH_2-\overset{\overset{*}{O}}{\overset{||}{C}}-O^-$
   (c) $CH_3CH_2-\overset{*}{O}-H$
   (d) Both (a) and (b)

9. In the given Ellingham diagram, X, Y and Z represent graph for metal oxides. At temperature below 983 K



   (a) Y will reduce oxide Z
   (b) Y will reduce oxide X
   (c) Z will reduce oxide X
   (d) Z will reduce oxide Y.

10. Which one of the following represents the correct increasing order of bond angles in the given molecules?
(a) $H_2O < OF_2 < OCl_2 < ClO_2$
(b) $OCl_2 < ClO_2 < H_2O < OF_2$
(c) $OF_2 < H_2O < OCl_2 < ClO_2$
(d) $ClO_2 < OF_2 < OCl_2 < H_2O$

11. Predict the order of Δ_o for the following compounds :
I. $[Fe(H_2O)_6]^{2+}$
II. $[Fe(CN)_2(H_2O)_4]$
III. $[Fe(CN)_4(H_2O)_2]^{2-}$
(a) (I) < (II) < (III)
(b) (II) < (I) < (III)
(c) (III) < (II) < (I)
(d) (II) < (III) < (I)

12. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as
(a) an enamine (b) a Schiff's base
(c) an amine (d) an imine.

13. Which of the following is aromatic?
(a) [10]-Annulene (b) [14]-Annulene
(c) [16]-Annulene (d) [18] -Annulene

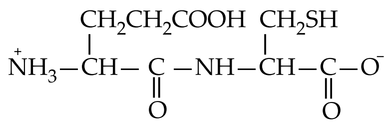
14. The electronegativities of H and Cl are 2.1 and 3.0 respectively. The correct statement about the nature of HCl is
(a) 17% ionic (b) 83% ionic
(c) 50% ionic (d) 100% ionic.

15. Identify I, II and III for the given reactions sequence.
$$FeCr_2O_4 \xrightarrow{I} Na_2CrO_4 \xrightarrow{II} Na_2Cr_2O_7 \xrightarrow{III} Na_2Cr_2O_4$$

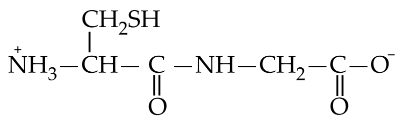
	I	II	III
(a)	Na_2CO_3/air, Δ	H_2SO_4	C
(b)	NaOH/air, Δ	C, Δ	C, Δ
(c)	Na_2CO_3/air, Δ	C, Δ	C, Δ
(d)	NaOH/air, Δ	Al, Δ	C, Δ

16. 1.325 g sample of fertilizer is heated with H_2SO_4 and then treated with alkali. The gas evolved is passed into 50.0 mL of 0.2030 N H_2SO_4. 25.32 mL of 0.1980 N NaOH are required for the titration of unused acid. The percentage of nitrogen in the fertilizer is
(a) 5.30% (b) 5.43%
(c) 4.99% (d) 6.01%

17. A tripeptide (*X*) on partial hydrolysis gave two dipeptides *Cys-Gly* and *Glu-Cys*, *i.e.*,



Glu-Cys

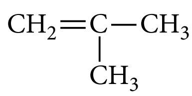
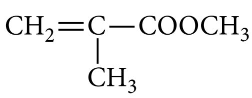
and 

Cys-Gly

Identify the tripeptide.
(a) *Glu-Cys-Gly* (b) *Gly-Glu-Cys*
(c) *Cys-Gly-Glu* (d) *Cys-Glu-Gly*

18. Which is not correct?
(a) $Ge(OH)_2$ is amphoteric.
(b) $GeCl_2$ is more stable than $GeCl_4$.
(c) GeO_2 is weakly acidic.
(d) $GeCl_4$ in HCl forms $[GeCl_6]^{2-}$ ion.

19. The enthalpy change involved in the oxidation of glucose is -2880 kJ mol^{-1}. 25% of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one km, what is the maximum distance that a person will be able to walk after eating 120 g of glucose?
(a) 4.80 km (b) 5.25 km
(c) 3.80 km (d) 5.75 km

20. Elastol is a polymer used to cleanup oil spill. It is a non-toxic, non-dispersant chemical. One gallon can remove 150 gallons of heavy oil. The monomer of elastol is
(a) $CH_2{=}CH{-}CN$ (b) 
(c) 
(d) $CH_2{=}CH{-}Ph$

21. Which of the following reagents reacts differently with HCHO, CH_3CHO and CH_3COCH_3?
(a) HCN (b) NH_2NH_2
(c) NH_2OH (d) NH_3

22. *Fac-mer* isomerism is associated with which one of the following complexes?

(a) $[M(AA)_2]$ (b) $[MA_3B_3]$
(c) $[M(AA)_3]$ (d) $[MABCD]$

23. Which of the following ions, derive from cyclooctatetraene (COT) by adding or removing a suitable number of π-electrons, are aromatic?

$C_8H_8^+$	$C_8H_8^{2+}$	$C_8H_8^-$	$C_8H_8^{2-}$
I	II	III	IV

(a) I, II (b) II, IV (c) III, IV (d) II, III

24. Ammonia forms complexes with Ag^+ ion according to the following reactions :

(i) $[Ag(H_2O)_2]^+_{(aq)} + NH_{3(aq)} \rightleftharpoons [Ag(NH_3)(H_2O)]^+_{(aq)} + H_2O_{(l)}$

(ii) $[Ag(NH_3)(H_2O)]^+_{(aq)} + NH_{3(aq)} \rightleftharpoons [Ag(NH_3)_2]^+_{(aq)} + H_2O_{(l)}$

The equilibrium constants for the reaction (i) and (ii) are 2.0×10^3 and 8.3×10^3 respectively, then the equilibrium constant of the following reaction is

$[Ag(H_2O)_2]^+_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Ag(NH_3)_2]^+_{(aq)} + 2H_2O_{(l)}$

(a) 4.15×10^6 (b) 2.0×10^3
(c) 8.3×10^3 (d) 16.6×10^6

25. In spite of being an odd-electron molecule, ClO_2 does not dimerise because

(a) the odd electron is delocalised
(b) the odd electron is localised on the chlorine atom
(c) the two Cl – O bonds do not have the same length
(d) of $p_x - p_x$ bonding in the chlorine atom.

26. During the preparation of arenediazonium salts, the excess of nitrous acid is destroyed by adding

(a) aq. NaOH (b) aq. Na_2CO_3
(c) aq. NH_2CONH_2 (d) aq. KI.

27. Which of the following is a non-hypnotic tranquilizer?

(a) Chlordiazepoxide (b) Meprobamate
(c) Equanil (d) All of these

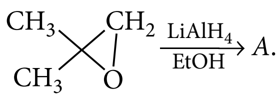
28. The Schrodinger wave equation for hydrogen atom is

$$\psi_{2s} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$$

where, a_0 is Bohr's radius. Let the radial node in 2*s* be at r_0 then the value of *r* in terms of a_0 is

(a) $r = a_0/2$ (b) $2r = a_0$
(c) $r = 2a_0$ (d) $r = a_0$

29. Identify the product (*A*) in the given reaction,



(a) $(CH_3)_2CHCH_2OH$ (b) $CH_3CH_2CH_2CH_2OH$
(c) $(CH_3)_3COH$ (d) $CH_3CHOHCH_2CH_3$

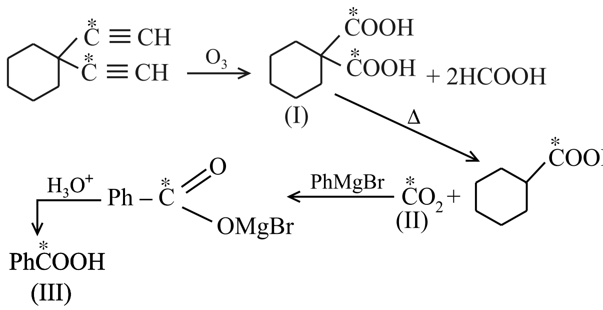
30. The correct formula of permanganic acid is

(a) $HMnO_4$ (b) $HMnO_5$
(c) H_2MnO_4 (d) H_2MnO_3

SOLUTIONS

1. (b)

2. (b) :



3. (d) : $2H_2SO_4 + NO + NO_2 \longrightarrow 2NO{\cdot}HSO_4 + H_2O$

4. (a) : $Cu^{2+} + e^- \rightarrow Cu^+$; $\Delta G_1^\circ = -0.15$ F

$In^{2+} + e^- \rightarrow In^+$; $\Delta G_2^\circ = +0.40$ F

$In^+ \rightarrow In^{3+} + 2e^-$; $\Delta G_3^\circ = -0.84$ F

$\therefore$ $Cu^{2+} + In^{2+} \rightarrow Cu^+ + In^{3+}$; $\Delta G^\circ = -0.59$ F

$\Delta G^\circ = -nFE^\circ = -0.59$ F

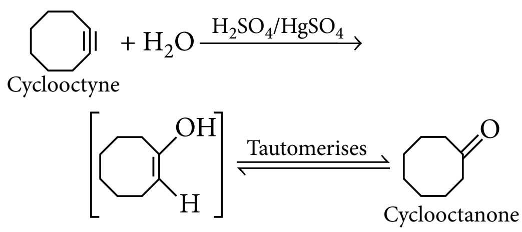
or $-1 \times E^\circ_{cell} F = -0.59$ F $\therefore$ $E^\circ_{cell} = 0.59$ V

At equilibrium, $E^\circ_{cell} = \dfrac{0.0591}{n}\log K_c$

$\therefore$ $0.59 = \dfrac{0.0591}{1}\log K_c$

Hence, $K_c = \text{antilog}\left(\dfrac{0.59}{0.0591}\right) = 10^{10}$

5. (d) :



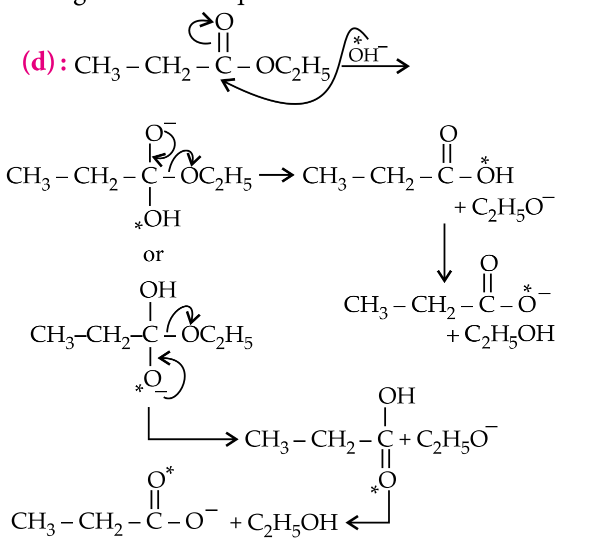
6. **(b) :** $A \rightarrow B;\ k_1 = 10^{10}e^{-20000/T}$
$C \rightarrow D;\ k_2 = 10^{12}e^{-24606/T}$

When, $k_1 = k_2$

$$10^{10}e^{-20000/T} = 10^{12}e^{-24606/T}$$
$$e^{4606/T} = 100$$
$$\frac{4606}{T} = 2.303 \log 100 = 2.303 \times 2$$
$$\therefore\quad T = \frac{4606}{2.303\times 2} = 1000\ \text{K}$$

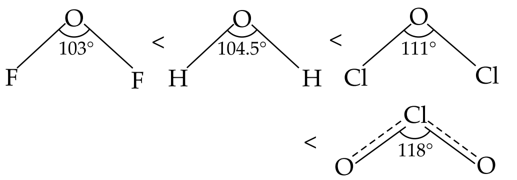
7. **(b) :** Truncated octahedron has 14 faces, 8 regular hexagonals and 6 squares.

8. **(d) :**



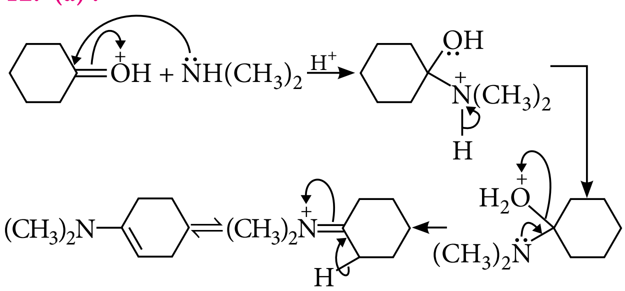
9. **(a) :** $\Delta G°$ of Y is less than Z and hence, it will reduce oxide of Z.

10. **(c) :**



11. **(a) :** The value of Δ_o for mixed ligands depends on the additive contributions of the ligand strengths. Since, CN^- has greater ligand strength than H_2O, the strength increases as the number of CN^- ions increases. Hence, the correct order of Δ_o is III > II > I.

12. **(a) :**



13. **(d) :** [18]-Annulene is aromatic since it is planar and contains $(4n + 2)$ π-electrons. Although annulenes [10] and [14] also contain $(4n + 2)$ π-electrons but the crowding of hydrogens inside the ring prevents planarity and hence are not aromatic.

14. **(a) :** % ionic character $= 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$
$= 16(3.0 - 2.1) + 3.5(3.0 - 2.1)^2$
$= 14.4 + 2.835 = 17.235 \approx 17\%$

15. **(a) :**

$$\underbrace{4FeCr_2O_4 + 8Na_2CO_3 + 7O_2}_{\text{(I)}} \xrightarrow{\Delta} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

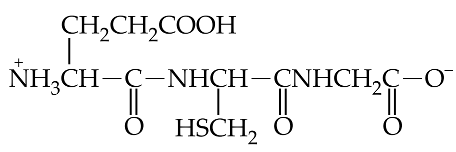
$$2Na_2CrO_4 \xrightarrow{H_2SO_4\text{(II)}} Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

$$Na_2Cr_2O_7 \xrightarrow{3C\text{(III)}} 3CO + Na_2Cr_2O_4$$

16. **(b) :** Weight of sample $(W) = 1.325$ g
Volume of acid (H_2SO_4) used $(V_1) = 50$ mL
Normality of acid $(N_1) = 0.2030$ N
Volume of alkali required $(V_2) = 25.32$ mL
Normality of alkali $(N_2) = 0.1980$ N
Milliequivalents of H_2SO_4 left after reaction with NH_3 = Milliequivalents of alkali used for neutralisation of rest $H_2SO_4 = N_2V_2 = 0.1980 \times 25.32 = 5.013$
Milliequivalents of H_2SO_4 taken to absorb $NH_3 = N_1V_1$
$= 0.2030 \times 50 = 10.15$
$\therefore$ Milliequivalents of H_2SO_4 which has reacted with $NH_3(x)$ = Milliequivalents of acid taken – Milliequivalents of acid left
$= 10.15 - 5.013 = 5.137$

$$\text{Now, \% N} = \frac{1.4x}{W} = \frac{1.4\times 5.137}{1.325} = 5.43\%$$

17. **(a) :** Since the tripeptide on hydrolysis gave two dipeptides *Glu-Cys* and *Cys-Gly*. Hence, cystine must be in between glutamic acid and glycine.



Glu-Cys-Gly

18. **(b) :** Ge^{4+} is more stable than Ge^{2+}, thus $GeCl_4$ is more stable than $GeCl_2$.

19. (a) : Molar mass of glucose ($C_6H_{12}O_6$) = 180 g mol^{-1}

Combustion reaction of glucose can be written as

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}; \quad \Delta H = -2880 \text{ kJ mol}^{-1}$$

Number of moles of 120 g of glucose

$$= \frac{120 \text{ g}}{180 \text{ g mol}^{-1}} = \frac{2}{3} \text{ mol}$$

Enthalpy available from 120 g of glucose

$$= \frac{2}{3} \times 2880 = 1920 \text{ kJ}$$

Enthalpy available for muscular work $= 1920 \times \frac{25}{100}$

$$= 480 \text{ kJ}$$

Distance to which a person can move

$$= \left(\frac{1 \text{ km}}{100 \text{ kJ}}\right) \times 480 \text{ kJ} = 4.80 \text{ km}$$

20. (b) : Elastol is a polymer of 2-methylpropene.

21. (d) : NH_3 reacts differently. With HCHO, it gives urotropine, with acetaldehyde, it gives $CH_3CH{=}NH$ and with acetone, it gives diacetone amine.

22. (b)

23. (b) : Removal of two electrons from COT (cyclooctatetraene), gives cyclic species II ($C_8H_8^{2+}$) which has 6 π-electrons and hence is aromatic. Similarly, addition of two electrons to COT gives a cyclic species IV ($C_8H_8^{2-}$) which has 10 π-electrons and hence is also aromatic.

24. (d) :
$$[Ag(H_2O)_2]^+_{(aq)} + NH_{3(aq)} \rightleftharpoons [Ag(NH_3)(H_2O)]^+_{(aq)} + H_2O_{(l)} \quad ...(1)$$
$$K_1 = 2.0 \times 10^3$$

$$K_1 = \frac{[Ag(NH_3)(H_2O)]^+_{(aq)}}{[Ag(H_2O)_2]^+_{(aq)}[NH_{3(aq)}]} \quad ...(i)$$

$$[Ag(NH_3)(H_2O)]^+_{(aq)} + NH_{3(aq)} \rightleftharpoons [Ag(NH_3)_2)]^+_{(aq)} + H_2O_{(l)} \quad ...(2)$$
$$K_2 = 8.3 \times 10^3$$

$$K_2 = \frac{[Ag(NH_3)_2]^+_{(aq)}}{[Ag(NH_3)(H_2O)]^+_{(aq)}\ [NH_{3(aq)}]} \quad ...(ii)$$

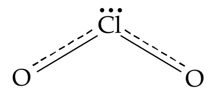
$$[Ag(H_2O)_2]^+_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Ag(NH_3)_2]^+_{(aq)} + 2H_2O_{(l)} \quad ...(3)$$

$$K = \frac{[Ag(NH_3)_2]^+_{(aq)}}{[Ag(H_2O)_2]^+_{(aq)}[NH_{3(aq)}]^2} \quad ...(iii)$$

From equations (i), (ii) and (iii), it is clear that

$K = K_1K_2 = 2 \times 10^3 \times 8.3 \times 10^3 = 16.6 \times 10^6$

25. (a) : The odd electron of Cl_2 is delocalised thus, ClO_2 does not dimerise.



26. (c) : Urea decomposes HNO_2 to N_2, CO_2 and H_2O.

$$NH_2CONH_2 + 2HONO \rightarrow 2N_2\uparrow + CO_2\uparrow + 3H_2O$$

27. (d)

28. (c) : ψ^2_{2s} = probability of finding electrons within 2*s* sphere.

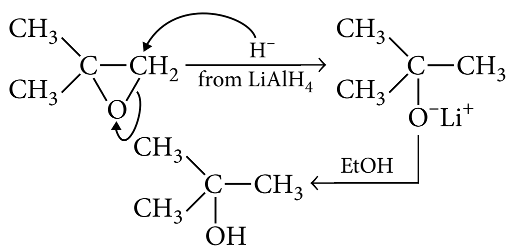
$\psi^2_{\text{at node}} = 0$ (probability of finding an electron is zero at node)

$\therefore\ r = r_0$

$$\text{So, } \psi^2 = 0 = \frac{1}{32\pi}\left[\frac{1}{a_0}\right]^3\left[2 - \frac{r}{a_0}\right]^2 \times e^{-\frac{r}{a_0}}$$

$$\text{or} \quad \left[2 - \frac{r}{a_0}\right] = 0 \quad \Rightarrow \quad 2 = \frac{r}{a_0} \quad \text{or} \quad r = 2a_0$$

29. (c) : In the basic medium, the reaction occurs by S_N2 mechanism and the nucleophile, *i.e.*, H^- ion (from $LiAlH_4$) attacks the smaller alkyl group.



30. (a)

PRACTICE PAPER

NEET

Exam on
6^{th} May 2018

1. Compressibility factor (Z) for N_2 at $-50\ °C$ and 800 atm pressure is 1.95. Calculate the number of moles of N_2 gas required to fill a gas cylinder of 100 mL capacity under the given conditions.
   (a) 2.24 (b) 1.12
   (c) 6.10 (d) 2.90

2. Benzaldehyde reacts with ammonia to form
   (a) hydrobenzamide (b) benzamide
   (c) aniline (d) phenyl cyanide.

3. Which of the following is not a property of hydrophilic sols?
   (a) High concentration of dispersed phase can be easily attained.
   (b) Coagulation is reversible.
   (c) Viscosity and surface tension are nearly same as that of water.
   (d) The charge of the particle depends on the pH value of the medium; it may be positive, negative or even zero.

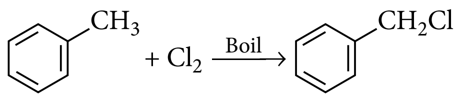
4. Which of the following alcohols is most reactive with HCl in the presence of $ZnCl_2$?
   (a) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$ (b) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$
   (c) $CH_3-\underset{\underset{CH_3}{|}}{CH}-OH$ (d) CH_3OH

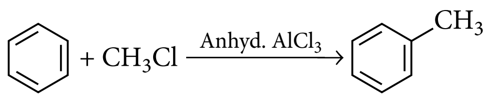
5. A ball of mass 200 g is moving with a velocity of 10 m sec^{-1}. If the error in measurement of velocity is 0.1%, the uncertainty in its position is
   (a) 3.32×10^{-31} m
   (b) 3.34×10^{-27} m
   (c) 5.32×10^{-25} m
   (d) 2.64×10^{-32} m

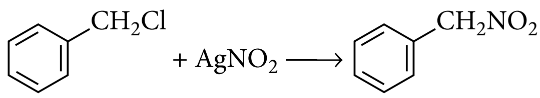
6. When neopentyl bromide is subjected to Wurtz reaction, the product formed is
   (a) 2, 2, 4, 4-tetramethylhexane
   (b) 2, 2, 4, 4-tetramethylpentane
   (c) 2, 2, 5, 5-tetramethylhexane
   (d) 2, 2, 3, 3-tetramethylhexane.

7. Which of the following statements about primary amines is false?
   (a) Aryl amines react with nitrous acid to produce nitrophenols.
   (b) Alkyl amines are stronger bases than ammonia.
   (c) Alkyl amines are stronger bases than aryl amines.
   (d) Alkyl amines react with nitrous acid to produce alcohols.

8. $NaNO_3$ when decomposes above 800 °C does not give
   (a) N_2 (b) O_2 (c) NO_2 (d) Na_2O

9. Which of the following is a free radical substitution reaction?
   (a) 

   (b) 

   (c) 

   (d) $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$

10. The density of sodium borohydride is 1.074 g/cm^3. 3.91 g of sodium borohydride contains 2.50×10^{23} atoms of H. The number of moles of H atoms present in 28.0 cm^3 of sodium borohydride is
    (a) 3.192 (b) 2.03
    (c) 1.67 (d) 1.92

11. The resistance of 0.5 N solution of an electrolyte in a conductivity cell was found to be 25 ohm. Calculate the equivalent conductivity of the solution if the electrodes in the cell are 1.6 cm apart and have an area of 3.2 cm^2.
(a) 10 S cm^2 equiv (b) 15 S cm^2 equiv
(c) 20 S cm^2 equiv (d) 40 S cm^2 equiv

12. The volume strength of 1.5 N H_2O_2 solution is
(a) 4.8 (b) 8.4 (c) 3.0 (d) 8.0

13. Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125 pm. What is the length of the side of unit cell?
(a) 145 pm (b) 353.5 pm
(c) 125 pm (d) 250 pm

14. The gases that give rise to photochemical smog are
(a) oxides of sulphur (b) oxides of nitrogen
(c) oxides of carbon (d) oxygen.

15. Identify the final product (Z) in the following sequence of reactions :
$$(CH_3)_2CO + HCN \longrightarrow X \xrightarrow{H_3O^+} Y \xrightarrow[\text{Heat}]{H_2SO_4} Z$$
(a) $(CH_3)_2C(OH)COOH$
(b) $CH_2{=}C(CH_3)COOH$
(c) $HOCH_2CH(CH_3)COOH$
(d) $CH_3CH{=}CHCOOH$

16. Calculate the longest wavelength (in Å) which can remove the electron from first Bohr's orbit.
(Given : E_1 = 13.6 eV)
(a) 303.81 (b) 912.24 (c) 1095.12 (d) 1215.67

17. The product of acid catalysed hydration of 2-phenyl propene is
(a) 3-phenyl-2-propanol (b) 1-phenyl-2-propanol
(c) 2-phenyl-2-propanol (d) 2-phenyl-1-propanol.

18. Which of the following statements is not true about glucose?
(a) It is an aldohexose.
(b) On heating with HI it forms n-hexane.
(c) It is present in furanose form.
(d) It does not give 2,4-DNP test.

19. In a system : $A_{(s)} \rightleftharpoons 2B_{(g)} + 3C_{(g)}$, if the concentration of C at equilibrium is increased by a factor 2, it will cause the equilibrium concentration of B to change by
(a) two times of its original value
(b) one half of its original value
(c) $2\sqrt{2}$ times of its original value
(d) $\frac{1}{2\sqrt{2}}$ time of its original value.

20. Which of the following statements is not true?
(a) The Ellingham diagram shows the plots of ΔG vs T.
(b) In froth floatation process, depressants are added to enhance the formation of froth.
(c) Extraction of zinc oxide is done by coke.
(d) CO is more effective reducing agent below 983 K.

21. In a mixture of A and B, components show –ve deviations as
(a) ΔV_{mix} is +ve
(b) A–B interactions are weaker than A–A and B–B interactions
(c) ΔH_{mix} is +ve
(d) A–B interactions are stronger than A–A and B–B interactions.

22. Out of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe), which one is expected to have the highest second ionisation enthalpy?
(a) V (b) Cr (c) Mn (d) Fe

23. In a first order reaction, the initial amount of a substance becomes 1/3 in 100 seconds. How much time will be taken to reduce the concentration to 1/9 of the initial concentration?
(a) 200 sec (b) 100 sec (c) 50 sec (d) 400 sec

24. Among the following halides :
1. BCl_3 2. $AlCl_3$ 3. $GaCl_3$ 4. $InCl_3$
the order of decreasing Lewis acid character is
(a) 1, 2, 3, 4 (b) 4, 3, 2, 1
(c) 3, 4, 2, 1 (d) 2, 3, 4, 1.

25. Which of the following statements is not true about low density polythene?
(a) Obtained through free radical addition
(b) Chemically inert and tough
(c) Good conductor of electricity
(d) Highly branched structure

26. Identify a reagent from the following which can easily distinguish between but-1-yne and but-2-yne.
(a) Bromine, CCl_4
(b) H_2, Lindlar's catalyst
(c) Dilute H_2SO_4, $HgSO_4$
(d) Ammoniacal Cu_2Cl_2 solution

27. Which of the following is paramagnetic in nature?
(a) $[Cr(CO)_6]$ (b) $[Fe(CO)_5]$
(c) $[Fe(CN)_6]^{4-}$ (d) $[Cr(NH_3)_6]^{3+}$

28. Which of the following contains maximum number of lone pairs of electrons on the central atom?
(a) ClO_3^- (b) XeF_4
(c) SF_4 (d) I_3^-

29. Match List I with List II and select the correct option.

List I	List II
(I) Iodoform	(A) Anaesthetic
(II) Methyl salicylate	(B) Antiseptic
(III) Diethyl ether	(C) Insecticide
(IV) Hexachlorocyclohexane	(D) Detergent
	(E) Pain balm

(a) I - B, II - E, III - C, IV - D
(b) I - D, II - B, III - A, IV - C
(c) I - B, II - E, III - A, IV - C
(d) I - C, II - A, III - D, IV - B

30. In group 14, the inert-pair effect is more prominent in
(a) tin and lead (b) carbon and silicon
(c) carbon and lead (d) none of these.

31. Which is the most suitable reagent for the following conversion?

$$CH_3-CH=CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \longrightarrow CH_3-CH=CH-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

(a) Tollens' reagent
(b) Benzoyl peroxide
(c) I_2 and NaOH solution
(d) $LiAlH_4/C_2H_5OH$

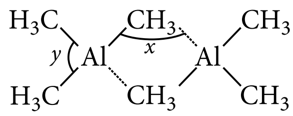
32. The values of T_c for few gases are given below : H_2 : 33.2 K, O_2 : 154.3 K, He : 5.3 K and CO_2 : 304.10 K. What is the correct increasing order of liquefaction of the above gases?
(a) $He < O_2 < H_2 < CO_2$
(b) $He < H_2 < O_2 < CO_2$
(c) $CO_2 < O_2 < H_2 < He$
(d) $O_2 < CO_2 < H_2 < He$

33. The basic character of the transition metal monoxides follows the order
(a) CrO > VO > FeO > TiO
(b) TiO > FeO > VO > CrO
(c) TiO > VO > CrO > FeO
(d) VO > CrO > TiO > FeO

34. 0.316 g of an organic compound, after heating with fuming nitric acid and barium nitrate crystals in a sealed tube gave 0.466 g of the precipitate of barium sulphate. The percentage of sulphur in the compound is
(a) 1.125 (b) 20.25
(c) 15.85 (d) 30.15

35. Nitrogen oxide that does not contain N—N bond is
(a) N_2O (b) N_2O_3 (c) N_2O_4 (d) N_2O_5

36. Compare x and y bond angles for the given molecule :



(a) $x > y$ (b) $y > x$
(c) $x = y$ (d) $x \geq y$

37. In context with the transition elements, which of the following statements is incorrect?
(a) In addition to the normal oxidation states, zero oxidation state is also shown by elements in complexes.
(b) In the highest oxidation states, transition elements show basic character and form cationic complexes.
(c) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.
(d) Once the d^5 configuration is exceeded, the tendency to involve all the 3d electrons in bonds decreases.

38. Enantiomers have
(a) identical m.pt./b.pt. but different refractive indices
(b) identical m.pt./b.pt. and refractive indices but rotate plane polarised light in opposite directions but to the same extent
(c) different refractive indices and rotate plane polarised light in the same direction but to different extent
(d) different m.pt./b.pt. but rotate plane polarised light in different directions but to the same extent.

39. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. Density of sodium chloride is
(a) 1.08 g cm^{-3} (b) 2.16 g cm^{-3}
(c) 3.24 g cm^{-3} (d) none of these.

40. Some properties of the two species, NO_3^- and H_3O^+ are described below. Which one of them is correct?
(a) Dissimilar in hybridisation for the central atom with different structures.
(b) Isostructural with same hybridisation for the central atom.
(c) Isostructural with different hybridisation for the central atom.

(d) Similar in hybridisation for the central atom with different structures.

41. The plot of $\log_{10}K$ vs $1/T$ leads to a straight line having intercept equal to

(a) $\Delta G°$ (b) $\frac{\Delta G°}{2.303R}$

(c) $\frac{\Delta S°}{2.303R}$ (d) $\frac{\Delta H°}{2.303R}$

42. Which of the following complexes has magnetic moment of 2.83 B.M.?

(a) $[Ni(NH_3)_6]^{2+}$ (b) $[Ni(CN)_4]^{2-}$

(c) $TiCl_4$ (d) $[CoCl_6]^{3-}$

43. The final product of the following sequence of reactions

$CaO + C \xrightarrow{\text{Heat}} A \xrightarrow{H_2O} B$, is

(a) ethanol

(b) ethyl hydrogen sulphate

(c) acetylene (d) ethylene glycol.

44. The same quantity of electricity that liberated 2.158 g of Ag was passed through a gold salt, and 1.314 g of gold was deposited. The equivalent mass of Ag is 107.9. Calculate oxidation state of Au in the salt. (At. mass of Au = 197)

(a) +2 (b) +3 (c) +1 (d) 0

45. If $E°_{M^+/M} = -1.2$ V, $E°_{X_2/X^-} = 1.1$ V and $E°_{O_2/H_2O} = 1.23$ V, then on electrolysis of aqueous solution of salt MX, the products obtained are

(a) M, X_2 (b) H_2, X_2 (c) H_2, O_2 (d) M, O_2

SOLUTIONS

1. (a) : We have, $Z = \frac{PV}{nRT}$

$\therefore$ Mole of $N_2(n) = \frac{PV}{ZRT} = \frac{800 \times 100}{1.95 \times 0.0821 \times 223 \times 1000}$

$= 2.24$

2. (a) :

$$\begin{matrix} C_6H_5-CH=\boxed{O + H_2}N\boxed{H} \\ C_6H_5-CH=\boxed{O + H_2}N\boxed{H} \end{matrix} + \boxed{O}=CHC_6H_5$$

$$\longrightarrow \begin{matrix} C_6H_5CH=N \\ C_6H_5CH=N \end{matrix} > CHC_6H_5 + 3H_2O$$

Hydrobenzamide

3. (c) : Hydrophilic sols have lower surface tension and higher viscosity than that of water.

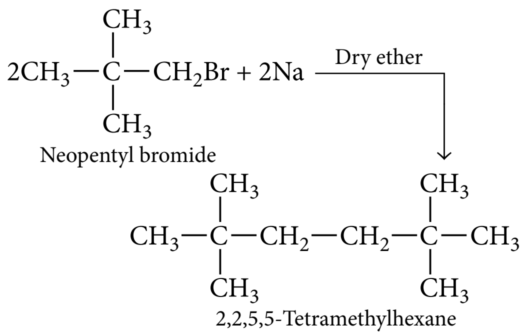
4. (a) : Order of reactivity of alcohols towards Lucas reagent : 3° > 2° > 1°

5. (d) : $\Delta v = \frac{0.1}{100} \times 10 = 10^{-2}$ m sec^{-1};

Now, $\Delta v \cdot \Delta x = \frac{h}{4\pi m}$

$\Delta x = \frac{6.625 \times 10^{-34}}{4 \times 10^{-2} \times 3.14 \times 200 \times 10^{-3}} = 2.64 \times 10^{-32}$ m

6. (c) :



7. (a)

8. (c) : $NaNO_3 \xrightarrow{500\,°C} NaNO_2 + \frac{1}{2}O_2$

$2NaNO_3 \xrightarrow{>800\,°C} Na_2O + N_2 + \frac{5}{2}O_2$

9. (a) : Side chain chlorination takes place in the presence of heat or light by free radical substitution mechanism.

10. (a) : Weight of sodium borohydride in 28.0 cm^3

$= 28 \times 1.074 = 30.072$ g

$\because$ 3.91 g of sodium borohydride has moles of H atoms

$= \frac{2.50 \times 10^{23}}{6.023 \times 10^{23}}$

$\therefore$ 30.072 g of sodium borohydride has moles of H atoms $= \frac{2.50 \times 10^{23}}{6.023 \times 10^{23}} \times \frac{30.072}{3.91}$

$= 3.192$ moles of H atoms

11. (d) : $\rho = R \cdot \frac{a}{l} = \frac{25 \times 3.2}{1.6} = 50$

$\kappa = \frac{1}{\rho} = \frac{1}{50} = 0.02$

$\Lambda_{eq} = \kappa \times V = \kappa \times \frac{1000}{\text{Normality}} = \frac{0.02 \times 1000}{0.5}$

$= 40$ S cm^2 equiv.

12. (b) : Volume strength = 5.6 × Normality

= 5.6 × 1.5 = 8.4

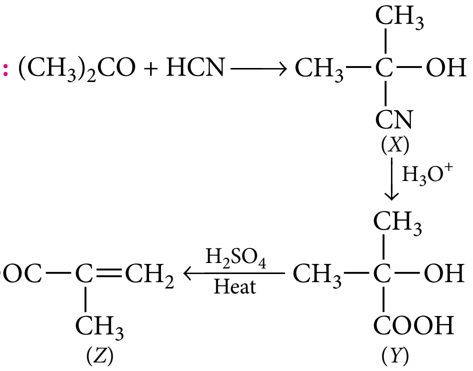
13. (b) : For a cubic close packed structure, length of the side of unit cell is related to radius as,

$r = \frac{a}{2\sqrt{2}}$

$a = r \times 2\sqrt{2} = 125 \times 2 \times 1.414$ pm $= 353.5$ pm

14. (b)

15. (b) :



16. (b) : The photon capable of removing electron from first Bohr's orbit must possess energy

$= 13.6 \text{ eV} = 13.6 \times 1.602 \times 10^{-19}$ J

$= 21.787 \times 10^{-19}$ J

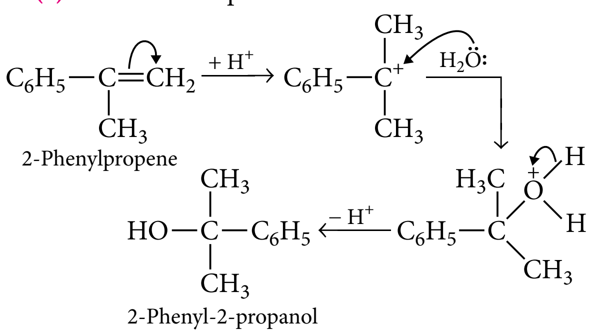
$\because \quad E = \dfrac{hc}{\lambda}$

$21.787 \times 10^{-19} = \dfrac{6.625 \times 10^{-34} \times 3.0 \times 10^8}{\lambda}$

$\therefore \quad \lambda = 912.24 \times 10^{-10} \text{ m} = 912.24$ Å

This is longest λ because a photon having λ higher than this will possess energy lesser than required, as $E \propto \dfrac{1}{\lambda}$.

17. (c) : The reaction proceeds via carbocation formation.



18. (c) : Glucose is present in pyranose form.

19. (d) : $A_{(s)} \rightleftharpoons 2B_{(g)} + 3C_{(g)}$

$\therefore \quad K_c = [C]^3[B]^2;$

If $[C]$ becomes twice, let conc. of B becomes B', then

$K_c = [2C]^3[B']^2$ or $[C]^3[B]^2 = [2C]^3[B']^2$

$\therefore \quad \dfrac{[B']}{[B]} = \sqrt{\dfrac{1}{8}} = \dfrac{1}{2\sqrt{2}}$

20. (b)

21. (d) : Option (d) is a required condition for negative deviation along with $\Delta V_{mix} = -\text{ve}$ and $\Delta H_{mix} = -\text{ve}$.

22. (b) : The electronic configurations of these elements are

V $(Z = 23)$: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^3\, 4s^2$

Cr $(Z = 24)$: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^5\, 4s^1$

Mn $(Z = 25)$: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^5\, 4s^2$

Fe $(Z = 26)$: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^6\, 4s^2$

In the case of chromium, the second electron has to be removed from the half-filled *d*-shell which is more stable.

23. (a) : For the first order reaction,

$k = \dfrac{2.303}{t} \log_{10} \dfrac{a}{(a-x)}$

Let the initial amount is a mol L^{-1}, then

after $t = 100$ seconds, $(a - x) = \dfrac{a}{3}$ mol L^{-1}

$\therefore \quad k = \dfrac{2.303}{100} \log_{10} \dfrac{a}{a/3} = \dfrac{2.303}{100} \log_{10} 3$

$= 10.988 \times 10^{-3}$ sec^{-1}

Let the time required to reduce the concentration to $a/9$ is t_1, then

$t_1 = \dfrac{2.303}{10.988 \times 10^{-3}} \log_{10} \dfrac{a}{a/9} = 200$ sec

24. (a)

25. (c) : It is not a good conductor of electricity.

26. (d) : 1-Alkynes react with ammoniacal solution of Cu_2Cl_2 to form red precipitate of the corresponding copper alkynides.

But-1-yne reacts with ammoniacal Cu_2Cl_2 as follows :

$CH_3-CH_2-C\equiv CH + Cu(NH_3)_2Cl$

$\longrightarrow \underset{\text{red precipitate}}{CH_3-CH_2-C\equiv C^-Cu^+}$

But, but-2-yne does not react with this reagent.

27. (d) : CO and CN^- are strong field ligands which force the electrons to pair up and thus, complex is generally diamagnetic. NH_3 is a weak field ligand so that electrons remain unpaired and complex is generally paramagnetic.

28. (d) : ClO_3^- : 1 lone pair

XeF_4 : 2 lone pairs

SF_4 : 1 lone pair

I_3^- : 3 lone pairs

29. (c) : Iodoform - Antiseptic

Methyl salicylate - Pain balm

Diethyl ether - Anaesthetic

Hexachlorocyclohexane - Insecticide

30. (a) : Inert pair effect increases as we move down the group.

31. (c)

32. (b) : Higher the value of T_c, more easily the gas can be liquified.

33. (c) : The size of given metals decreases whereas ionization enthalpy increases from Ti to Fe. Hence, the metallic character of the metals decreases and therefore, basicity of oxides decreases from Ti to Fe.

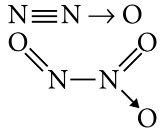
34. (b) : Mass of substance taken = 0.316 g
Mass of $BaSO_4$ formed = 0.466 g
From stoichiometry, $\underset{233}{BaSO_4} \equiv \underset{32}{S}$
($\because$ molecular mass of $BaSO_4 = 137 + 32 + 64 = 233\ g\ mol^{-1}$)

Then, mass of S in 0.466 g of $BaSO_4 = \dfrac{0.466 \times 32}{233}$ g

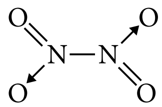
Percentage of S in the compound $= \dfrac{0.466 \times 32}{233} \times \dfrac{100}{0.316}$
$= 20.25\ \%$

35. (d) : N_2O $\quad N\equiv N \rightarrow O$

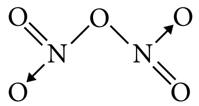
N_2O_3



N_2O_4



N_2O_5



36. (b)

37. (b) : In highest oxidation states, transition metals cannot form cationic complexes. Also, they show acidic character because in highest oxidation state, they can only accept the electrons and form anionic complexes.

38. (b)

39. (b) : $\rho_{NaCl} = \dfrac{Z \times M}{a^3 \times N_A}$

$\because$ $Z = 4$, formula mass $(M) = 58.5$, $a = 5.64 \times 10^{-8}$ cm

$\therefore$ $\rho = \dfrac{4 \times 58.5}{6.023 \times 10^{23} \times (5.64 \times 10^{-8})^3} = 2.16\ g\ cm^{-3}$

40. (a) : No. of electron pairs at the central atom
= no. of atoms bonded to it + 1/2[group number of central atom – valency of the central atom ± no. of electrons]
No. of electron pairs at the central atom

in $NO_3^- = 3 + \frac{1}{2}[5 - 6 + 1] = 3$ $\quad$ (sp^2 hybridisation).

No. of electron pairs at the central atom in

in $H_3O^+ = 3 + \frac{1}{2}[6 - 3 - 1] = 4$ $\quad$ (sp^3 hybridisation).

41. (c) : $\Delta G° = -2.303\ RT \log_{10} K$

$$\log_{10} K = -\frac{\Delta G°}{2.303\,RT} = -\frac{(\Delta H° - T\Delta S°)}{2.303\,RT}$$
$$= -\frac{\Delta H°}{2.303\,RT} + \frac{\Delta S°}{2.303\,R}$$

Comparing it with straight line equation,
$y = mx + c$

we get, slope $(m) = \dfrac{-\Delta H°}{2.303\ R}$

and intercept $(c) = \dfrac{\Delta S°}{2.303\ R}$

42. (a) : 2.83 B.M. implies two unpaired electrons according to the expression, $\mu = \sqrt{n(n+2)}$ B.M. The species Ni^{2+}, Ni^{2+}, Ti^{4+} and Co^{3+} in the given complexes have $3d^8$, $3d^8$, $3d^0$, and $3d^6$ electronic configurations, respectively. CN being a strong field ligand causes pairing of electrons thus, $[Ni(CN)_4]^{2-}$ has zero unpaired electrons with dsp^2 hybridisation, while NH_3 being a weak field ligand, does not cause pairing of electrons thus, $[Ni(NH_3)_6]^{2+}$ has two unpaired electrons and 2.83 B.M. magnetic moment.

43. (c) : $CaO + 2C \xrightarrow{Heat} \underset{(A)}{CaC_2} \xrightarrow{H_2O} \underset{(B)}{CH\equiv CH}$

44. (b) : Number of equivalents of gold deposited
= number of equivalents of silver deposited

i.e., $\dfrac{W_{gold}}{E_{gold}} = \dfrac{W_{silver}}{E_{silver}}$

$$E_{gold} = \frac{E_{silver} \times W_{gold}}{W_{silver}} = \frac{107.9 \times 1.314}{2.158} = 65.7$$

Equivalent mass $= \dfrac{\text{Atomic mass}}{\text{Oxidation no. of Au in salt}}$

Thus, ox. no. of Au $= \dfrac{\text{Atomic mass}}{E_{gold}} = \dfrac{197}{65.7} = 3$

45. (b) : $MX \longrightarrow M^+ + X^-$
$H_2O \longrightarrow H^+ + OH^-$

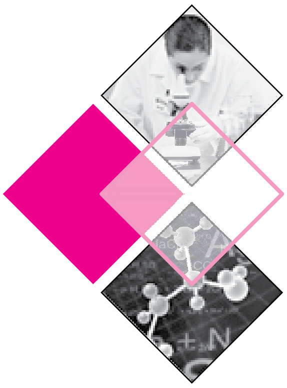
At cathode : H^+ ions will get reduced as the standard reduction potential of M^+ ions is negative (less than that of H^+).

$2H^+ + 2e^- \longrightarrow H_2$

At anode : The species having low value of standard reduction potential are oxidised. Hence, the reaction at anode is

$2X^- \longrightarrow X_2 + 2e^-$

$\therefore$ The products obtained are H_2 at cathode and X_2 at anode.



CONCEPT BOOSTER

Dear students! Thank you all a lot for the feedback that you have given for the last article. This is the last part of Organometallic Compounds. Hopefully, this will fulfil the requirement of COMPETITIVE EXAMINATIONS you are going to face. Moreover, some more problems will be given in upcoming issues. Do read the basics of every chapter very carefully. Do take care, all the best!

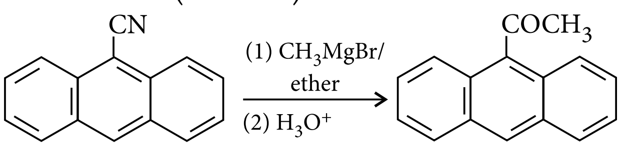
*Arunava Sarkar

A BRIEF OVERVIEW OF ORGANOMETALLIC REAGENTS AND ORGANOMETALLIC CHEMISTRY

GRIGNARD REAGENTS

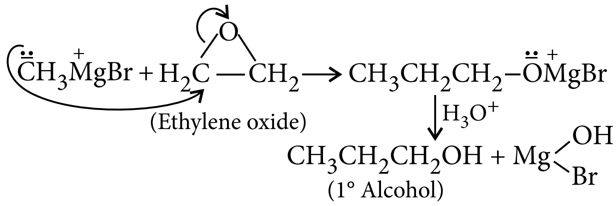
❍ Reaction with nitriles

Remember the basic idea here which is, whereever –CN group is connected, remove it from there and add $-COCH_3$ $\left(\text{or } -\underset{\underset{O}{\|}}{C}-R\right)$.

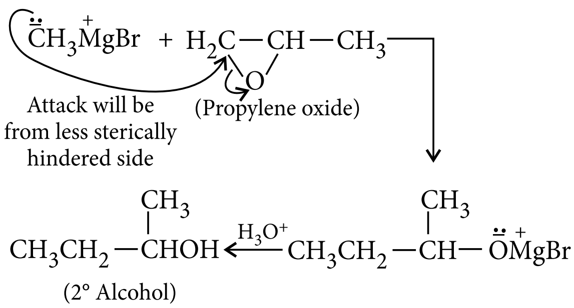


[$-CH_3$ or $-R$ comes from Grignard reagent]

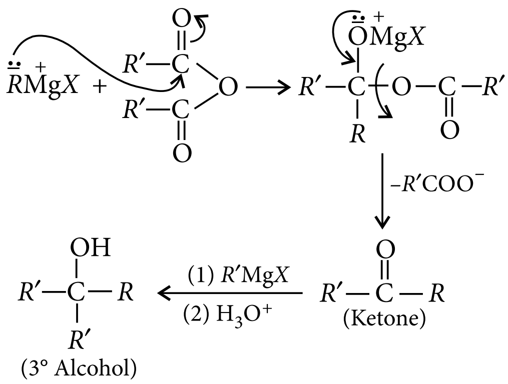
❍ Reaction with epoxide



If you use substituted epoxide, then you can also get 2° alcohol.



❍ Reaction with acid anhydride



❍ Reaction with alkyl halide

Reaction between Grignard reagent and an alkyl halide is often carried out very slowly as Grignard reagent is prepared from alkyl halide. So, the reaction between Grignard reagent and alkyl halide is carried out in presence of transition metal catalyst, specifically cobalt chloride ($CoCl_2$). This kind of transition metal catalysed reaction is known as Kharasch reaction. For example,

$$CH_3MgBr + CH_3CH_2Br \xrightarrow{CoCl_2} \underset{(\approx 68\%\text{-}70\%)}{CH_3CH_2CH_3}$$

It has been found that a reaction is possible in between Grignard reagent and α-haloketone. For example,

$$C_6H_5COCH_2Cl + C_6H_5MgBr \xrightarrow[\text{(2) ice cold HCl}]{\text{(1) dry ether, –28 °C}} C_6H_5COCH_2C_6H_5$$

*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

ORGANOLITHIUM COMPOUNDS

Obviously, organolithium compounds are characterised by a C – Li bond. Li is less electronegative than carbon and hence, the polarisation of carbon-lithium bond is shown as below :

$$>\overset{\delta-}{C}-\overset{\delta+}{Li}$$

Organolithium compounds are more reactive than Grignard reagents, however the nature of reaction remains the same in most of the cases and in some cases distinctly different.

Preparation of organolithium compounds

- **From alkyl or aryl halides**

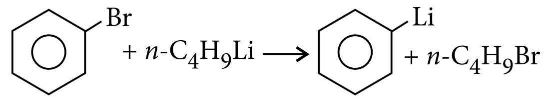
  $$R\text{—}X + 2Li \xrightarrow[\text{organic solvent}]{\text{low temperature}} R\text{—}Li + LiX$$
  $$\text{inert atmosphere (Ar)}$$

  Order of reactivity : $R - I > R - Br > R - Cl$

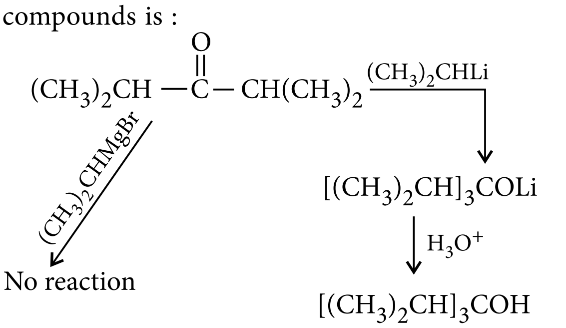
- **Halogen-metal exchange**

  $$R\text{—}X + R'Li \longrightarrow R\text{—}Li + R'\text{—}X$$

  e.g.,



  An important reaction to show the difference in reactivity between Grignard reagent and organolithium compound before getting into discussion on the reactions shown by organolithium compounds is :



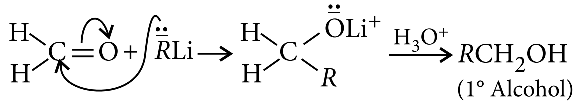
  So, organolithium compounds are more reactive than organomagnesium compounds.

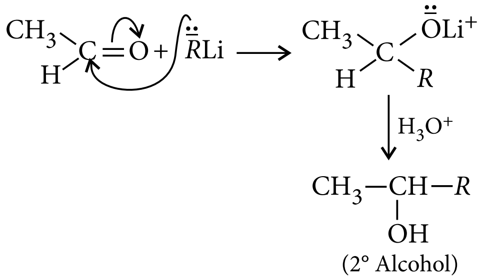
Most useful reactions of organolithium compounds

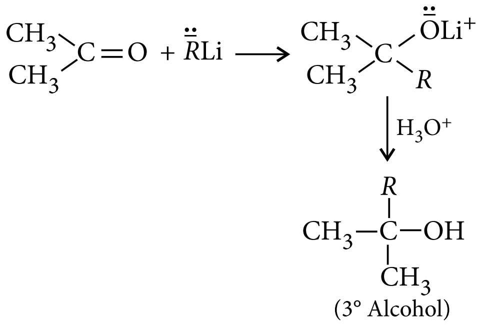
- **Reaction with carbonyl compounds (with the focus on conjugated carbonyl compounds)**

  Let us start the discussion with the similarities in the reactions with Grignard reagent.

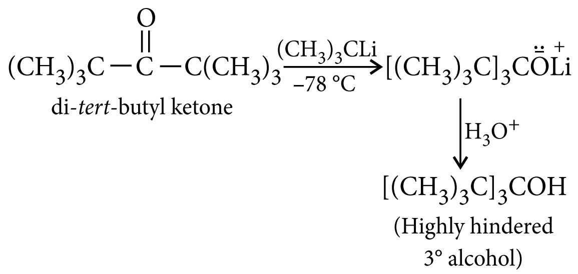
  Grignard reagent reacts with formaldehyde to give 1° alcohol (after hydrolysis), acetaldehyde to give 2° alcohol (after hydrolysis), acetone to give 3° alcohol (after hydrolysis). Same goes with organolithium compounds.



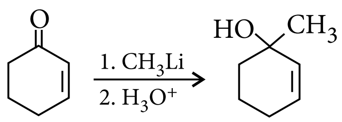




For the third case, there is a well known advantage of using organolithium compounds over Grignard reagents that is Grignard reagents do not react with hindered ketones but organolithium compounds do. Here is the best and most used example :



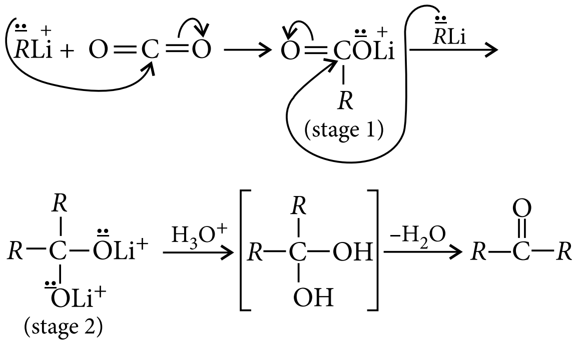
Now, let us take the case of α,β-unsaturated carbonyl compounds. We have seen that with α, β-unsaturated compounds, Grignard reagent can give either 1,2-addition or 1,4-addition product depending on the overall steric hindrance whereas organolithium compounds on the other hand, give exclusively 1,2-addition products.



[The reason for this is that organolithium compounds are aggressive nucleophiles.]

However, lithium dialkyl cuprates give exclusively 1,4-addition product.

- **Reaction with carbon dioxide**



So, here is an important difference with the Grignard reagent. In case of Grignard reagent, the reaction stops at stage 1 *i.e.*, 1 mole addition of Grignard reagent but in case of organolithium compounds, the reaction goes upto stage 2 *i.e.*, 2 moles addition of organolithium compound.

- **Electrophilic displacement**

$$R-X + R'Li \longrightarrow RLi + R'-X$$

A specific example of this kind can be given :

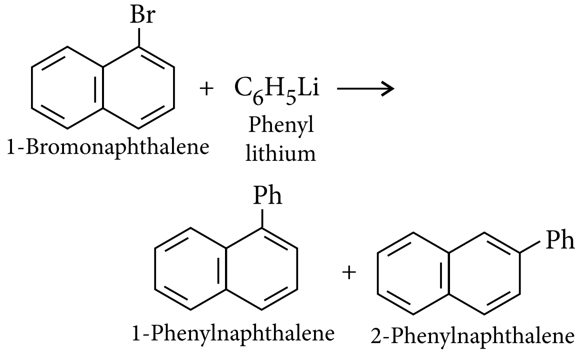
$$\underset{\text{Vinyl bromide}}{CH_2{=}CHBr} + \underset{n\text{-Butyl lithium}}{nC_4H_9Li} \longrightarrow CH_2{=}CHLi + nC_4H_9Br$$

- **Nucleophilic displacement**

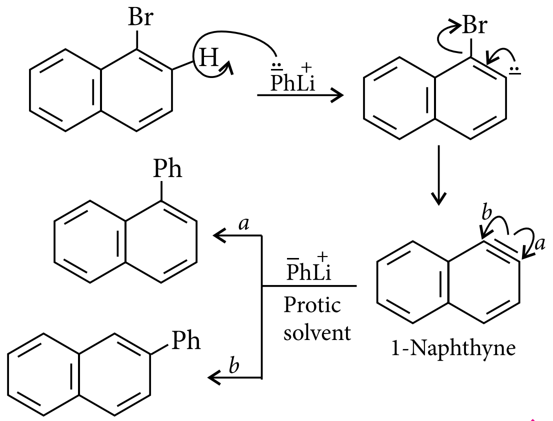
Here, a similar reaction as happens in Wurtz reaction takes place.

$$R-X + \ddot{R}'^{-}Li^{+} \xrightarrow[\text{path}]{S_N2} R-R' + LiX$$

It is to be remembered that in case of substitution in aromatic rings, elimination-addition reaction takes place. Take the following example,



Mechanism :



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CONCEPT MAP
CLASS XI

ESSENTIAL CONCEPTS OF ORGANIC CHEMISTRY

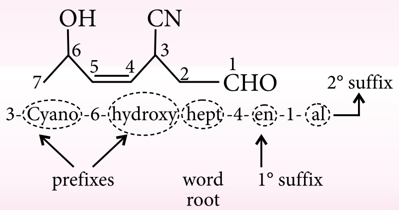
Get well-prepared for exams with quick revision of important concepts of organic chemistry.

Organic Chemistry - Some Basic Principles and Techniques

IUPAC Nomenclature

IUPAC name = prefixes + word root + 1° suffix + 2° suffix

e.g.,



Order of Species Showing Inductive Effect

- **–I-effect :** $R_3\overset{+}{N}— > —NO_2 > —SO_2R > —CN > —COOH > —F > —Cl > —Br > —I > —OR > —COR > —OH > —C_6H_5 > —CH=CH_2 > —H$
- **+I-effect :** $(CH_3)_3C— > (CH_3)_2CH— > CH_3CH_2— > CH_3— > —D > —H$

Order of Species Showing Resonance or Mesomeric Effect

- **+R-effect :** —Cl, —Br, —I, $—NH_2$, —NH*R*, $—NR_2$, —NHCOR, —OH, —O*R*, —S*R*, —SH, $—OCH_3$, —OCOR
- **–R-effect :** $—NO_2$, —CN, $\rangle C=O$, —CHO, —COOH, —COOR

- Bond order in compounds which exhibit resonance

$$= \frac{\text{Total number of bonds between two atoms in all the structures}}{\text{Total number of resonating structures}}$$

Hyperconjugation

Number of hyperconjugating structures ∝ number of α-hydrogens ∝ stability ∝ 1/heat of hydrogenation ∝ polarity ∝ dipole moment ∝ 1/bond length

Stability of Free Radicals

- Stability of free radicals $\propto +I\text{-effect} \propto \frac{1}{-I\text{-effect}} \propto +R\text{-effect} \propto \frac{1}{-R\text{-effect}}$

$Ph_3\dot{C} > Ph_2\dot{C}H > Ph\dot{C}H_2 >$ Allyl > 3° > 2° > 1° > $\dot{C}H_3 > CH_2=\dot{C}H$

Stability of Carbocations

- Stability of carbocations $\propto +I\text{-effect} \propto \frac{1}{-I\text{-effect}} \propto +R\text{-effect} \propto \frac{1}{-R\text{-effect}}$

$Ph_3\overset{+}{C} > Ph_2\overset{+}{C}H > Ph\overset{+}{C}H_2 >$ Allyl > 3° > 2° > 1° > $\overset{+}{C}H_3$

Stability of Carbanions

- Stability of carbanions $\propto -I\text{-effect} \propto \frac{1}{+I\text{-effect}} \propto -R\text{-effect} \propto \frac{1}{+R\text{-effect}}$

$Ph_3\bar{C} > Ph_2\bar{C}H > Ph\bar{C}H_2 >$ Allyl > $\bar{C}H_3$ > 1° > 2° > 3°

Stability of Carbene

Triplet > Singlet

Thin Layer Chromatography

Retention factor (R_f)

$$= \frac{\text{Distance travelled by the compound from base line }(x)}{\text{Distance travelled by the solvent from base line }(y)}$$

Quantitative Analysis

(Liebig's combustion method)

- $\%\text{ of C} = \frac{12}{44} \times \frac{\text{mass of } CO_2 \text{ formed}}{\text{mass of compound taken}} \times 100$
- $\%\text{ of H} = \frac{2}{18} \times \frac{\text{mass of } H_2O \text{ formed}}{\text{mass of compound taken}} \times 100$

(Dumas method)

- $\%\text{ of N} = \frac{28}{22400} \times \frac{\text{vol. of } N_2 \text{ at STP}}{\text{mass of compound taken}} \times 100$
- $\%\text{ of N} = \frac{1.4 \times \text{normality of acid} \times \text{vol. of acid used}}{\text{mass of compound taken}}$

(Kjeldahl's method)

- $\%\text{ of N} = \frac{1.4 \times \text{molarity of acid} \times \text{vol. of acid used} \times \text{basicity of acid}}{\text{mass of compound taken}}$

(Carius method)

- $\%\text{ of Cl} = \frac{35.5}{143.5} \times \frac{\text{mass of AgCl formed}}{\text{mass of compound taken}} \times 100$
- $\%\text{ of Br} = \frac{80}{188} \times \frac{\text{mass of AgBr formed}}{\text{mass of compound taken}} \times 100$
- $\%\text{ of I} = \frac{127}{235} \times \frac{\text{mass of AgI formed}}{\text{mass of compound taken}} \times 100$
- $\%\text{ of S} = \frac{32}{233} \times \frac{\text{mass of } BaSO_4 \text{ formed}}{\text{mass of compound taken}} \times 100$

(Ignition method)

- $\%\text{ of P} = \frac{62}{222} \times \frac{\text{mass of } Mg_2P_2O_7 \text{ formed}}{\text{mass of compound taken}} \times 100$

(Iodine method)

- $\%\text{ of O} = \frac{32}{88} \times \frac{\text{mass of } CO_2 \text{ formed}}{\text{mass of compound taken}} \times 100$
- $\%\text{ of O} = \frac{5\times16}{2\times127} \times \frac{\text{mass of } I_2 \text{ formed}}{\text{mass of compound taken}} \times 100$

ESSENTIAL CONCEPTS OF PHYSICAL CHEMISTRY

Get well-prepared for exams with quick revision of important concepts of physical chemistry.

CONCEPT MAP
CLASS XII

Solid State

Packing efficiency

$$= \frac{\text{Volume occupied by two spheres in the unit cell}}{\text{Total volume of the unit cell}} \times 100$$

- Mass of the atoms of unit cell = Number of atoms in a unit cell (Z) × Mass of atom (M_{atom})
- Mass of one atom $= \frac{\text{Molar mass }(M)}{\text{Avogadro's constant }(N_A)}$
- Density (ρ) of unit cell of a cubic crystal $= \frac{ZM}{V \times N_A} = \frac{ZM}{a^3 N_A}$

- Bragg's equation : $2d \sin\theta = n\lambda$
- Number of octahedral voids = No. of particles present in the close packing
- Number of tetrahedral voids = 2 × No. of octahedral voids

Characteristics of Different Types of Unit Cells

Crystal	No. of atom(s)/ unit cell	Packing efficiency	C.No.	Relation in d, a and r
scc	1	52.4%	6	$r = d/2 = a/2$
bcc	2	68%	8	$r = d/2 = \sqrt{3}a/4$
fcc	4	74%	12	$r = d/2 = a/2\sqrt{2}$

Void	Radius Ratio
Triangular	$0.155 \le r^+/r^- < 0.225$
Tetrahedral	$0.225 \le r^+/r^- < 0.414$
Octahedral	$0.414 \le r^+/r^- < 0.732$
Body-centred cubic	$0.732 \le r^+/r^- < 1$

Solids on the Basis of Electrical Properties

- **Conductors :** Electrical conductivity, 10^4 to 10^7 $\text{ohm}^{-1}\,\text{m}^{-1}$
- **Insulators :** Electrical conductivity, 10^{-20} to 10^{-10} $\text{ohm}^{-1}\,\text{m}^{-1}$
- **Semiconductors :** Electrical conductivity, 10^{-6} to 10^4 $\text{ohm}^{-1}\,\text{m}^{-1}$
  - ***n*-type semiconductors :** Group 14 elements doped with group 15 elements, free electrons increase conductivity.
  - ***p*-type semiconductors :** Group 14 elements doped with group 13 elements, holes increase conductivity.

Solutions

- Molality $(m) = \frac{M}{\rho - \frac{MM_2}{1000}}$
- Molarity $(M) = \frac{n_1}{(n_1M_1 + n_2M_2)/\rho}$

- **Henry's law :** $p_A = K_H \cdot x_A$: K_H increases with increase of temperature implying that solubility decreases with increase of temperature at the same pressure.
- **Raoult's law :** $p_1 = p_1^\circ x_1$, this law is applicable only if the two components form a homogeneous mixture.
- **Dalton's law of partial pressure :** $p_{total} = p_1 + p_2 + \ldots\, p_n$ and for two components system, $p_{total} = p_1^\circ + (p_2^\circ - p_1^\circ)x_2$

Ideal and Non-ideal Solutions

Ideal Solutions	Non-ideal Solutions
$p_1 = x_1p_1^\circ$; $p_2 = x_2p_2^\circ$ $\Delta H_{mix} = 0$, $\Delta V_{mix} = 0$ $A - B$ interactions ≈ $A - A$ and $B - B$ interactions.	$p_1 \ne x_1p_1^\circ$; $p_2 \ne x_2\,p_2^\circ$ $\Delta H_{mix} \ne 0$, $\Delta V_{mix} \ne 0$ $A - B$ interactions ≠ $A - A$ and $B - B$ interactions.

Non-ideal Solutions Showing Positive and Negative Deviations from Raoult's Law

Solutions showing positive deviation	Solutions showing negative deviation
$A - B << A - A$ or $B - B$ interactions. $\Delta H_{mix} > 0$, $\Delta V_{mix} > 0$ $p_1 > p_1^\circ x_1$	$A - B >> A - A$ or $B - B$ interactions. $\Delta H_{mix} < 0$, $\Delta V_{mix} < 0$ $p_1 < p_1^\circ x_1$

Colligative Properties

- **Relative lowering of vapour pressure :** $(p_A^\circ - p_A)/p_A^\circ = x_B$
- **Elevation in boiling point :** $\Delta T_b = T_b - T_b^\circ = K_b m$
- **Depression in freezing point :** $\Delta T_f = T_f^\circ - T_f = K_f m$
- **Osmotic pressure :** $\pi = CRT = (n/V)RT$

van't Hoff Factor and its Significance

$$i = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligative property}}$$

- **For association of solute :** $nA \rightarrow (A)_n$
  Degree of association $(\alpha) = (1 - i)\, n/n - 1$; $i < 1$
- **For dissociation of solute :** $(A)_n \rightarrow nA$
  Degree of dissociation $(\alpha) = i - 1/n - 1$; $i > 1$
- **Modified colligative properties :**
  $p_A^\circ - p_A/p_A^\circ = ix_B$; $\Delta T_b = iK_b m$; $\Delta T_f = iK_f m$; $\pi = iCRT$

ADVANCED CHEMISTRY BLOC

(HYDROLYSIS)

Mukul C. Ray, Odisha

HYDROLYSIS AND HYDRATION

NOTE : In this article equations are intensionally not balanced.

If you are ready to consider hydration along with hydrolysis, you will be amazed to see a large number of important chemical reactions of your syllabus comes under this single banner.

In hydrolysis, bonds break during the reaction while in hydration simply water is added. In hydrolysis, you watch more than one product while in hydration, there is only one product unless a disproportionation takes place.

$$CCl_4 + H_2O \longrightarrow \text{No hydrolysis ordinarily}$$

Carbon fails to expand its octet to receive the donation of electron pair from H_2O to form required intermediate. However, carbon uses the third energy shell to expand its octet.

$$CCl_4 + \underset{\text{steam}}{H_2O} \xrightarrow[\text{catalyst}]{\Delta} COCl_2 + HCl$$

$$SiCl_4 + H_2O \longrightarrow Si(OH)_4 + HCl$$

$$SiF_4 + H_2O \longrightarrow H_2SiO_3 + HF$$

But HF subsequently reacts with SiF_4.

$$SiF_4 + 2HF \longrightarrow H_2SiF_6$$

SiH_4 is stable to water but rapidly hydrolysed by alkali.

$$SiH_4 + OH^- \longrightarrow SiO_4^{4-} + H_2$$

In SiH_4, the hydrogen carries a partial negative charge and in OH^-, it carries a partial positive charge. This facilitates the release of H_2.

$$GeH_4 + OH^-\ (30\%) \longrightarrow \text{No hydrolysis}$$

Polarity of H in both GeH_4 and OH^- is positive.

$$BF_3 + H_2O \longrightarrow H^+[BF_3(OH)]^-$$

No hydrolysis, rather an acid-base reaction takes place.

$$BCl_3 + H_2O \longrightarrow B(OH)_3 + HCl$$

The general rule is the central atom produces the oxyacid maintaining its oxidation state while the peripheral atom produces the hydra-acid.

$$AlCl_3 + H_2O \longrightarrow Al(OH)_3 + HCl$$

Again, $NF_3 + H_2O \longrightarrow$ No hydrolysis

N – F bond is too strong to break.

$$NCl_3 + H_2O \longrightarrow NH_3 + HOCl$$

(not HNO_2 and HCl)

Nitrogen has no room to accept electrons. Therefore, it is the Cl that accepts donated electrons.

$$PF_5 + H_2O \longrightarrow \text{No hydrolysis}$$

P – F bond is again too strong to cleave.

$$PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$$

$$PCl_5 + H_2O \longrightarrow H_3PO_4 + HCl$$

$$SF_6 + H_2O \longrightarrow \text{No hydrolysis}$$

Steric factor is the primary reason of the failure as there is no room for H_2O to approach cental S atom, which is crowded by six fluorine atoms.

$$\underset{\substack{\text{does not}\\ \text{exist}}}{SCl_6} + H_2O \not\longrightarrow \underset{\substack{\text{does not}\\ \text{exist either}}}{S(OH)_6} + HCl$$

The lower electronegativity of six Cl^- or six OH^- is responsible for non-existence of these compounds.

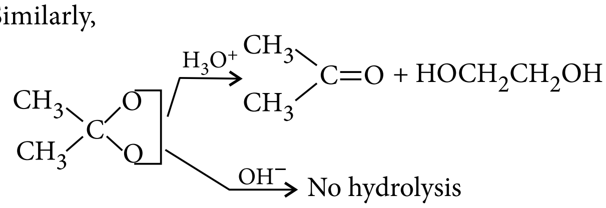
$$BiCl_3 + H_2O \longrightarrow \underset{\text{White turbidity}}{BiOCl} + HCl$$

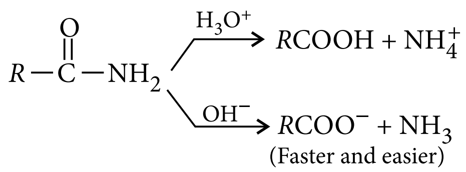
$$SbCl_3 + H_2O \longrightarrow \underset{\text{White turbidity}}{SbOCl} + HCl$$

There are BiO^+ and SbO^+ ions formed due to high positive charge density of Bi^{3+} and Sb^{3+} ions.

$$BrF_5 + H_2O \longrightarrow HBrO_3 + HF$$

Similarly,





$$R-\overset{\overset{\large O}{\|}}{C}-OR' \begin{cases} \xrightarrow{H_3O^+} RCOOH + R'OH \text{ (reversible)} \\ \xrightarrow{OH^-} RCOO^- + R'OH \text{ (irreversible)} \end{cases}$$

$$R-C\equiv N \begin{cases} \xrightarrow{H_3O^+} RCOOH + NH_4^+ \\ \xrightarrow{OH^-} RCOO^- + NH_3 \\ \xrightarrow[\text{hydrolysis}]{\text{partial}} RCONH_2 \end{cases}$$

$$R-\overset{+}{N}\equiv\overset{-}{C} \begin{cases} \xrightarrow{H_3O^+} R-\overset{+}{N}H_3 + HCOOH \\ \xrightarrow{OH^-} \text{No hydrolysis} \end{cases}$$

OH^- cannot attack either N or C.

$$R-O-R' \begin{cases} \xrightarrow{H_3O^+} R-OH + R'-OH \\ \xrightarrow{OH^-} \text{No hydrolysis} \end{cases}$$

RO^- or $R'O^-$ both are bad leaving groups.

$$CH_3-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-Br \begin{cases} \xrightarrow[H_2O]{Ag^+} (CH_3)_3C-OH(S_N1) \\ \xrightarrow[\Delta]{OH^-} CH_2=C\begin{matrix} CH_3 \\ CH_3 \end{matrix} \text{ No hydrolysis, rather elimination} \end{cases}$$

It is not surprising that sometimes hydrolysis reactions give a twist.

$$XeF_4 + H_2O \longrightarrow Xe + HF + O_2 + XeO_3$$

It is a clear cause of disproportionation during hydrolysis. Whereas, the other two fluorides of Xe behave in different ways :

$$XeF_2 + H_2O \longrightarrow Xe + HF + O_2$$
$$XeF_6 + H_2O \longrightarrow XeOF_4 + HF$$
$$XeOF_4 + H_2O \longrightarrow XeO_3 + HF$$

Before we close, check the following two reactions :

$$\begin{matrix} CH_3 \\ H \end{matrix}\!\!>C=NH \xrightarrow{H_2O} \begin{matrix} CH_3 \\ H \end{matrix}\!\!>C=O + NH_3$$

$$R-\overset{\overset{\large O}{\|}}{C}-Cl \xrightarrow{H_2O} R-\overset{\overset{\large O}{\|}}{C}-OH + HCl$$

No catalyst even required for these two organic reactions. We shall be checking hydration in the next episode.

◈◈

CHEMISTRY MUSING

SOLUTION SET 55

1. (d): $cis\text{-}X \underset{k_b}{\overset{k_f}{\rightleftharpoons}} trans\text{-}X$

Initial	a	0
at time t	$a - x$	x
at eqm	$a - x_e$	x_e

$$K_{(eq)} = \frac{k_f}{k_b}; k_b = \frac{3\times10^{-4}}{0.1} = 3\times10^{-3}$$

As we know $(k_f + k_b) = \frac{1}{t}\ln\left(\frac{x_e}{x_e - x}\right)$

Given, $x = \frac{x_e}{2}$ $\therefore$ $(k_f + k_b) = \frac{1}{t}\ln 2$

or $(3\times10^{-4} + 3\times10^{-3}) = \frac{0.693}{t}$

$\therefore$ $t = 210$ sec

2. (d): Average $C_{v,m} = \frac{n_1C_{v,m_1} + n_2C_{v,m_2}}{n_1 + n_2} = 2R$ ...(i)

For adiabatic process, $dU = dw$

$$n_1C_{v,m_1}dT + n_2C_{v,m_2}dT = -(n_1RT + n_2RT)\times\frac{dV}{V}$$

$$\frac{dT}{T} = -\frac{R}{\text{Average } C_{v,m}}\left(\frac{dV}{V}\right)$$

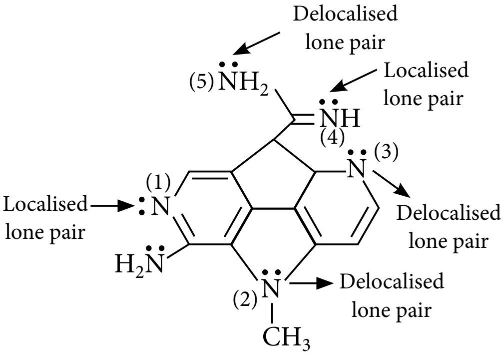
On substituting the value of average $C_{v,\,m}$ from eqn (i), then on integration, we get

$$\ln\frac{T_2}{T_1} = -\frac{1}{2}\ln\left(\frac{V_2}{V_1}\right) \Rightarrow T_2 = 320\times\left(\frac{1}{4}\right)^{1/2} = 160\text{ K}$$

$$\Delta U = (n_1C_{v,\,m_1} + n_2C_{v,\,m_2})\Delta T$$

$$= \left(1\times3R + 2\times\frac{3}{2}R\right)(160 - 320) = -960\,R$$

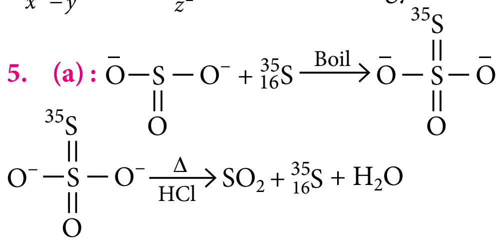
3. (b):



When the lone pair is delocalised and involved in resonance, *i.e.*, involved in more extended resonance then will be less available for protonation. Thus, the order of basicity is : 4 > 1 > 5 > 3 > 2.

4. (b): With glycinato ligand, Pt^{2+} and Pt^{4+} both show isomerism but with ethylene diamine, Pt^{2+} does not show but Pt^{4+} show isomerism. In $[Pt(en)_2]^{2+}$, Pt^{2+} is dsp^2 hybrid in square planar splitting $d_{x^2-y^2}$ has higher energy in comparison of d_{z^2} but in $[Pt(en)_3]^{4+}$, $d_{x^2-y^2}$ and d_{z^2} are at same energy level.

5. (a):



6. (b): For a constant volume process under adiabatic conditions,

$\Delta U = \Delta U_{\text{heating}} + \Delta U_{298\text{ K}} = 0$

Hence, $\Delta U_{\text{heating}} = -\Delta U_{298\text{ K}}$

$$= -\int_{298\text{ K}}^{T_f}\Sigma nC_v dT = -240.6\text{ kJ} \qquad ...(i)$$

Form IV

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For MTG Learning Media Pvt. Ltd.
Mahabir Singh
Director

Since, 2 moles unreacted N_2 are associated with 1/2 mole of O_2 ($\because$ Ratio of $N_2 : O_2$ in air = 4 : 1), we have

$\Sigma nC_v = C_v(H_2O, g) + 2C_v(N_2, g)$

$= (39.1 + 2 \times 26.4)\ J\ K^{-1} = 91.9\ J\ K^{-1}$

Hence, from eqn. (i), on integrating, we have

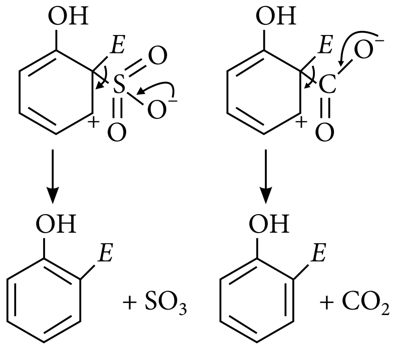
$91.9\ J\ K^{-1}\ (T_f - 298) = 240,600\ J$

$T_f - 298 = 240,600\ J/91.9\ J\ K^{-1} = 2618\ K$

$T_f = (2618 + 298)\ K = 2916\ K$

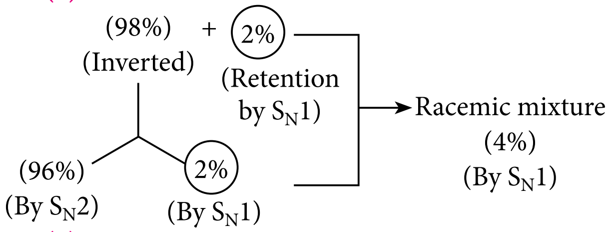
7. (c) : In case of G as EWG or EWG attached to *ortho*- or *para*-position with respect to group G, σ-complex (arenium ion) will be destabilised leading to decrease of rate of reaction for *ipso* substitution.

8. (c) :



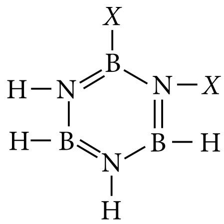
SO_3 and CO_2 are good leaving groups as formation of C = C and S = O bonds provides thermodynamic stability.

9. (4) :



10. (4) :

(i)



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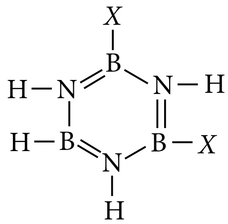

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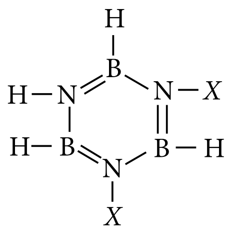
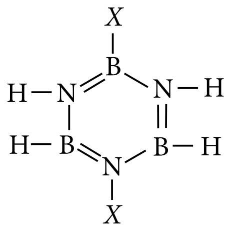


(iv)



NEET | JEE ESSENTIALS

Class XI

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Unit 9 Principles Related to Practical Chemistry

Practical work in labs improves the scientific knowledge and understanding of students, as well as providing opportunities for working scientifically and developing hands on skills.
Much of forensic science, medicine, pharmaceutical research and many chemical manufacturing processes, rely on accurate techniques and observations.

Quantitative Estimation

A quantitative analysis is one in which the amount or concentration of a particular species in a sample is determined accurately and precisely.

Titration

The process of addition of the known solution from the burette to the measured volume of solution of the substance to be estimated until the reaction between the two is just complete.

Titration

- **Unknown Solution**: The solution consisting of substance to be estimated is termed as titrate or unknown solution.
- **Standard Solution**
  - **Primary Standard**: These can be accurately weighed and their solutions are not to be standardised before use *e.g.*, oxalic acid, potassium dichromate, etc.
  - **Secondary Standard**: The solutions of these reagents are to be standardised before use as these cannot be weighed accurately *e.g.*, sodium hydroxide, hydrochloric acid, etc.

Acid-base titration

- When the strength of an acid is determined with the help of a standard solution of base, it is known as acidimetry.
- When the strength of a base is determined with the help of a standard solution of an acid, it is known as alkalimetry.

These titrations involve neutralisation of an acid with an alkali.

$$\underset{\text{Acid}}{HA} + \underset{\text{Alkali}}{BOH} \longrightarrow \underset{\text{Salt}}{BA} + \underset{\text{Water}}{H_2O}$$

Indicator

A substance which helps in physical detection of completion of the titration is called indicator.

Indicators

External Indicators

These indicators are not added in the reaction mixture. They are used outside the system *e.g.*, potassium ferricyanide is used in titration of Mohr's salt against potassium dichromate.

Internal Indicators

These indicators are added in the reaction mixture *e.g.*, in acid-base titration, methyl orange, methyl red and phenolphthalein.

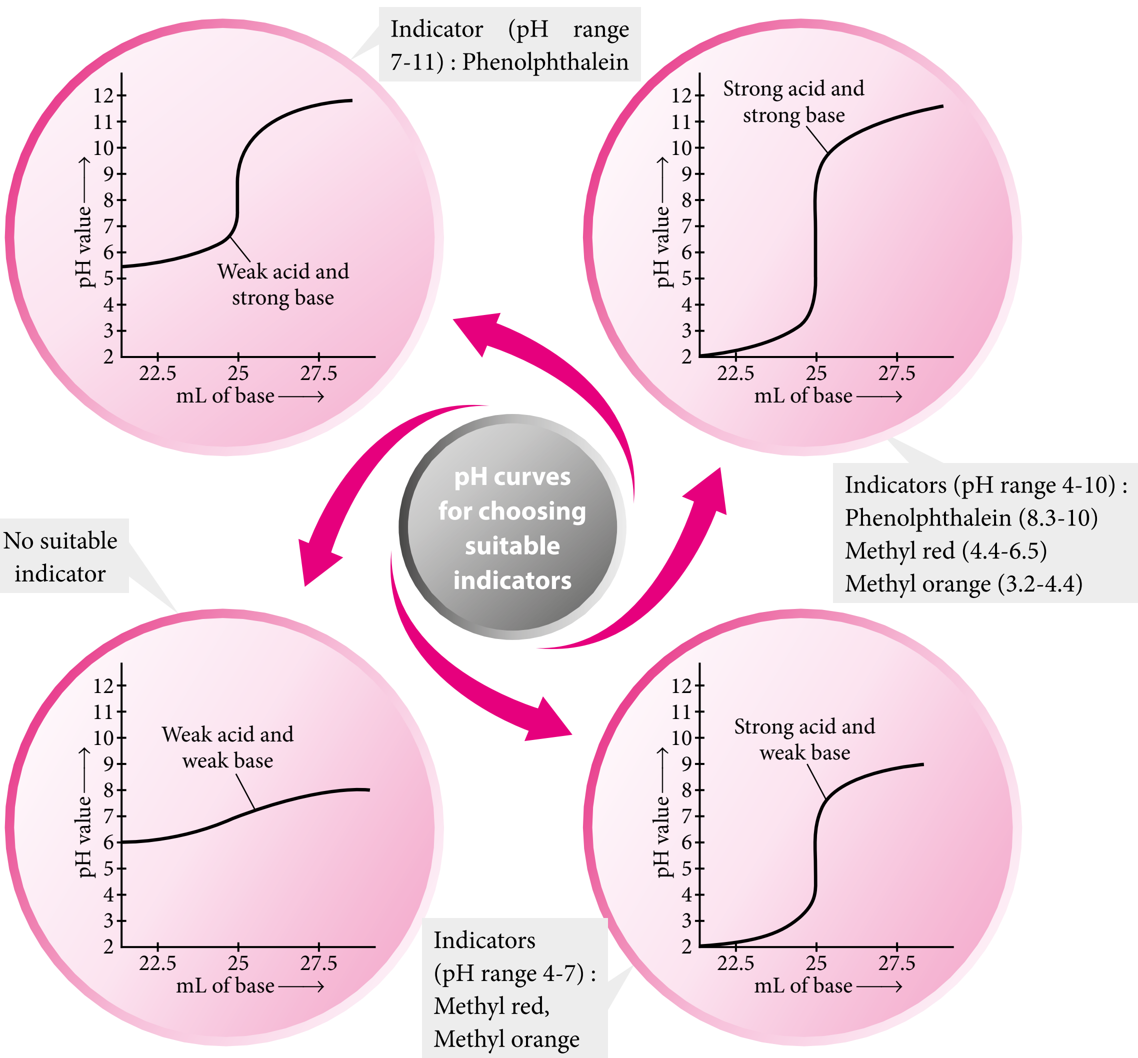
Self Indicators

These indicators themselves show colour change at the end of titration *e.g.*, in titration of oxalic acid against $KMnO_4$, $KMnO_4$ acts as self indicator.

How to choose a suitable indicator :

Indicator in a titration is selected on the basis of pH range at end point.

Indicator	pH-range	Colour of indicator	
		Acid	Alkaline
Phenolphthalein	8.3 – 10	Colourless	Pink
Methyl orange	3.2 – 4.4	Red	Yellow
Methyl red	4.4 – 6.5	Red	Yellow
Litmus	5.0 – 8.0	Red	Blue
Phenol red	6.8 – 8.4	Yellow	Red



Determination of Strength of NaOH

Principle : Strength of NaOH solution can be determined by titrating it against standard solution of oxalic acid.

$$\begin{matrix}COOH\\|\\COOH\end{matrix} + 2NaOH \rightarrow \begin{matrix}COONa\\|\\COONa\end{matrix} + 2H_2O$$

Indicator : Phenolphthalein

Preparation of standard solution :

$$\text{Oxalic acid}\left(\begin{matrix}COOH\\|\\COOH\end{matrix}\cdot 2H_2O\right)$$

$$\text{Equivalent weight} = \frac{126}{2} = 63$$

For preparing 250 mL solution of N/10 oxalic acid,

$$\text{weight required} = \frac{63\times\frac{1}{10}\times 250}{1000} = 1.575\text{ g}$$

Thus, for preparing N/10 oxalic acid, take 1.575 g of oxalic acid and make it upto 250 mL using distilled water.

Calculation :

$$\underset{\text{(Oxalic acid)}}{N_1V_1} = \underset{\text{(Caustic soda)}}{N_2V_2}$$

$$N_2 = \frac{N_1V_1}{V_2}$$

Strength of caustic soda = Normality × Equivalent weight = $(N_2 \times 40)$ g/L

Determination of Strength of HCl

Principle : When hydrochloric acid is titrated against Na_2CO_3 solution, strength of HCl can be determined.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2\uparrow$$

Indicator : Methyl orange

Preparation of standard solution :

$$\text{Eq. weight} = \frac{106}{2} = 53$$

For preparing 250 mL solution of N/10 Na_2CO_3,

$$\text{weight required} = \frac{53\times\frac{1}{10}\times 250}{1000} = 1.325\text{ g}$$

Calculation :

$$\underset{(Na_2CO_3)}{N_1V_1} = \underset{(HCl)}{N_2V_2} \quad ; \quad N_2 = \frac{N_1V_1}{V_2}$$

Strength of given HCl = Normality × Eq. weight of HCl

$= (N_2 \times 36.5)$ g/L

Qualitative Analysis

Qualitative analysis deals with the identification of various constituents present in a given material. For example, zinc blende contains zinc and sulphur in the form of Zn^{2+} and S^{2-} ions.

Preliminary Tests

Flame Test :

Salt with 1-2 drops of conc. HCl is introduced in the non-luminous (oxidising part) flame of the Bunsen burner using platinum wire.

$Cu^{2+} \xleftarrow{\text{Greenish blue}}$

$K^{+} \xleftarrow{\text{Lilac}}$

$Na^{+} \xleftarrow{\text{Golden yellow}}$

$\xrightarrow{\text{Brick red}} Ca^{2+}$

$\xrightarrow{\text{Apple green}} Ba^{2+}$

$\xrightarrow{\text{Crimson red}} Sr^{2+}$

Borax Bead Test :

- Borax is heated on a loop of Pt wire, colourless, glassy bead of sodium metaborate and boric anhydride is formed.

$$Na_2B_4O_7\cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy bead}}$$

- Coloured salts are then heated on the glassy bead, coloured metaborate is formed in the oxidising flame.

Colour of bead in oxidising flame	Ion indicated
Green in hot, blue in cold	Copper
Pinkish violet in both hot and cold	Manganese
Yellowish brown in hot and pale yellow in cold	Iron
Brown in hot and pale brown in cold	Nickel

Acidic Radicals

Anions are acidic radicals

First group
CO_3^{2-}, S^{2-}, SO_3^{2-}
CH_3COO^-,
$S_2O_3^{2-}$, NO_2^-
Reagent used : dil. HCl

Second group
Br^-, Cl^-, I^-
NO_3^-, $C_2O_4^{2-}$
Reagent used : conc. H_2SO_4

Third group
SO_4^{2-}, PO_4^{3-}
Reagent used : dil.H_2SO_4/ conc. H_2SO_4

First Group :

Salt + dil. HCl

Effervescence or evolution of gas shows presence of group I acidic radicals

Colourless gas with suffocating smell with yellow ppt. of sulphur $\xrightarrow{\text{Pass through } K_2Cr_2O_7}$ Blackish green solution $\longrightarrow S_2O_3^{2-}$ confirmed

Colourless gas with rotten egg smell (H_2S gas) $\xrightarrow{\text{Lead acetate}} \underset{\text{Black ppt.}}{PbS} \longrightarrow S^{2-}$ confirmed

Brown gas (NO_2) $\xrightarrow{\text{Starch iodide paper}}$ Blue $\longrightarrow$ NO_2^- confirmed

- Colourless, odourless gas (CO_2 gas) $\xrightarrow{\text{Lime water}} \underset{\text{Milky}}{CaCO_3}$ (CO_3^{2-} or HCO_3^- may be present)
- Confirmatory test for HCO_3^- & CO_3^{2-}

Salt + water $\rightarrow$ boil and pass through lime water

Lime water does not turn milky $\downarrow$ HCO_3^- confirmed

Lime water turns milky $\downarrow$ CO_3^{2-} confirmed

Colourless gas with vinegar smell (CH_3COO^- may be present) Salt solution + $FeCl_3$ (neutral) $\longrightarrow$ $\underset{\text{Blood red colour solution}}{(CH_3COO)_3Fe} \longrightarrow CH_3COO^-$ confirmed

Colourless gas with suffocating smell (SO_2) $\xrightarrow{\text{Heat and pass through } K_2Cr_2O_7}$ Solution turns green due to $Cr_2(SO_4)_3 \longrightarrow SO_3^{2-}$ confirmed

Second Group : Salt + conc. H_2SO_4

Effervescence or evolution of gases indicates the presence of group II acidic radicals.

Gas	Radical	Observations and Reactions
HCl (Colourless gas, pungent smell)	Chloride (Cl^-)	$\underset{\text{Salt}}{NaCl} + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$ $NH_4OH + HCl \rightarrow \underset{\text{White dense fumes}}{NH_4Cl}\uparrow + H_2O$
Br_2 (Brown fumes)	Bromide (Br^-)	$\underset{\text{Salt}}{NaBr} + H_2SO_4 \rightarrow NaHSO_4 + HBr$ $2HBr + H_2SO_4 \rightarrow \underset{\text{Brown}}{Br_2}\uparrow + 2H_2O + SO_2$
I_2 (Deep violet gas)	Iodide (I^-)	$\underset{\text{Salt}}{2KI} + 2H_2SO_4 \rightarrow 2KHSO_4 + 2HI$ $2HI + H_2SO_4 \rightarrow \underset{\text{Violet}}{I_2}\uparrow + SO_2 + 2H_2O$
NO_2 (Light brown gas, pungent smell)	Nitrate (NO_3^-)	$\underset{\text{Salt}}{NaNO_3} + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$ $4HNO_3 \rightarrow 2H_2O + \underset{\text{Light brown fumes}}{4NO_2}\uparrow + O_2\uparrow$
$CO + CO_2$ (Colourless, odourless gas)	Oxalate ($C_2O_4^{2-}$)	$\underset{\text{Salt}}{Na_2C_2O_4} + H_2SO_4 \rightarrow Na_2SO_4 + H_2C_2O_4$ $H_2C_2O_4 + H_2SO_4 \rightarrow \underset{\text{Burns with blue flame}}{CO} + \underset{\text{Turns lime water milky}}{CO_2} + H_2O$

INFOSHOTS

Determination of sulphate by conductometric titration!

Titrimetric methods are much faster, but a good indicator has not been found for sulphate titrations. However, because the relative concentrations of ions in solution change during titration sequence, monitoring conductivity during the progress of a titration produces a signal which can be used to indicate equivalence point. A conductometric titration protocol has been developed which is relatively rapid, inexpensive and can produce accurate results.

Confirmatory Tests for Group II

Confirmatory tests for acid radicals of group II

Nitrate (NO_3^-)

Brown ring test : On treating aqueous solution of salt with freshly prepared solution of ferrous sulphate and concentrated sulphuric acid, gives a brown ring at the junction of two liquids.

$$\underset{\text{Salt}}{NaNO_3} + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

$$[Fe(H_2O)_6]SO_4 + NO \longrightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5NO]SO_4} + H_2O$$

Oxalate ($C_2O_4^{2-}$)

On acidifying salt solution or sodium carbonate extract with acetic acid and on adding calcium chloride solution gives white precipitate.

$$\underset{\text{Salt}}{Na_2C_2O_4} + CaCl_2 \longrightarrow \underset{\text{White ppt.}}{CaC_2O_4\downarrow} + 2NaCl$$

Filter and dissolve the precipitate in dilute sulphuric acid and add few drops of potassium permanganate solution.

$$CaC_2O_4 + H_2SO_4 \longrightarrow H_2C_2O_4 + CaSO_4$$

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + [O] \longrightarrow 2CO_2 + H_2O$$

Pink colour discharge of $KMnO_4$ confirming presence of oxalate ion.

Chloride (Cl^-)

Chromyl chloride test :

$$\underset{\text{Salt}}{NaCl} + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

$$CrO_3 + 2HCl \longrightarrow \underset{\substack{\text{Chromyl chloride} \\ \text{(Red vapours)}}}{CrO_2Cl_2\uparrow} + H_2O$$

These vapours on passing through sodium hydroxide solution give yellow solution of sodium chromate.

$$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{Yellow colour}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

The yellow solution on neutralising with acetic acid and on addition of lead acetate gives yellow precipitate of lead chromate.

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow \underset{\text{Yellow ppt.}}{PbCrO_4\downarrow} + 2CH_3COONa$$

Iodide (I^-)

Layer test : On treating salt with dilute sulphuric acid, chloroform or carbon tetrachloride and chlorine water, gives violet coloured layer.

$$\underset{\text{Salt}}{2NaI} + Cl_2 \longrightarrow 2NaCl + I_2$$

$$I_2 + \text{Chloroform} \longrightarrow \text{Violet coloured layer}$$

Starch paper test :

$$I_2 + \text{Starch} \longrightarrow \underset{\text{Blue colour}}{I_2\text{-starch complex}}$$

Bromide (Br^-)

Layer test : On treating salt with dilute sulphuric acid, chloroform or carbon tetrachloride and chlorine water gives brown coloured layer.

$$\underset{\text{Salt}}{2NaBr} + Cl_2 \longrightarrow 2NaCl + Br_2$$

$$Br_2 + \text{Chloroform} \longrightarrow \text{Brown coloured layer}$$

Third Group : These anions are identified by their characteristic chemical reactions.

Salt $\xrightarrow[\text{dil. HCl}]{BaCl_2}$ $BaSO_4$ White ppt. (Insoluble in dil. HCl) $\downarrow$ SO_4^{2-} confirmed (Sulphate)

Salt $\xrightarrow[C_2H_5OH]{H_2SO_4}$ $(C_2H_5)_3BO_3$ Burns with green edged flame $\downarrow$ BO_3^{3-} confirmed (Borate)

Salt $\xrightarrow{\text{dil. } HNO_3 \text{ + ammonium molybdate}}$ $\underset{\text{(Canary yellow ppt.)}}{(NH_4)_3PO_4\cdot 12MoO_3} \rightarrow \underset{\text{(Phosphate)}}{PO_4^{3-}\text{confirmed}}$

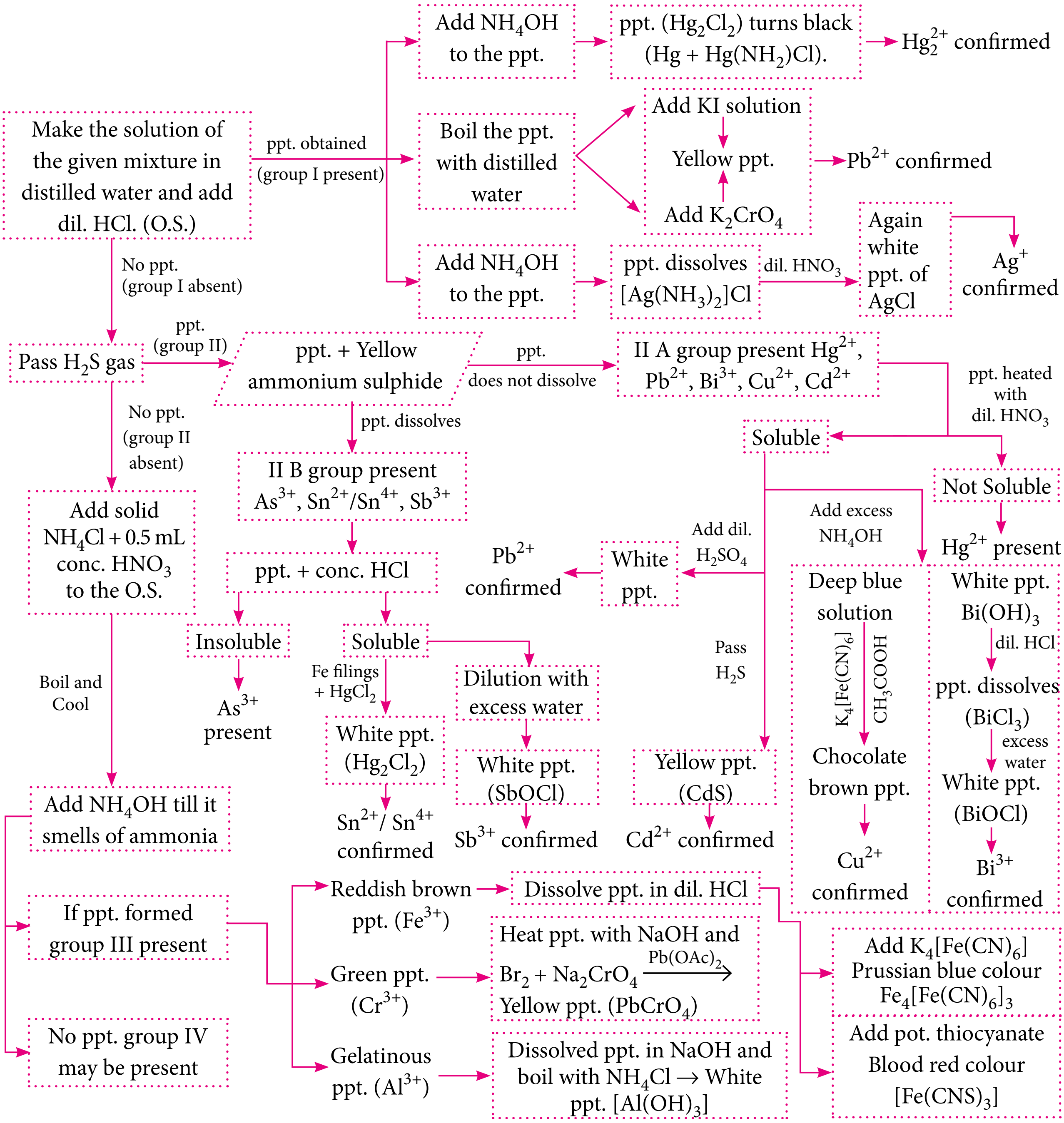
Basic Radicals

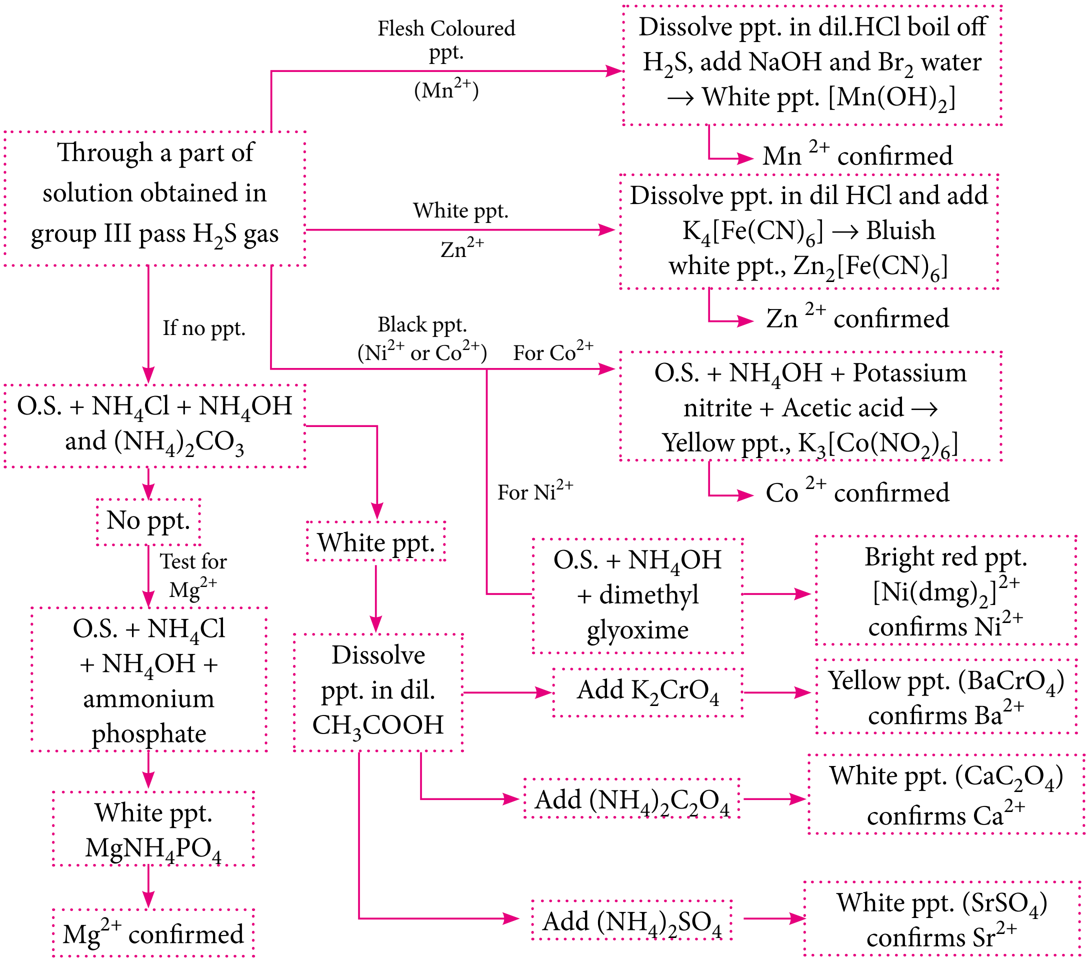
Cations are the basic radicals.

Group	Group reagent	Cations	Form of ppt.
I	dil. HCl	Pb^{2+}, Ag^+, Hg_2^{2+}	Chlorides
II	dil. HCl + H_2S gas	Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Sb^{3+}, As^{3+}, Sn^{2+}/Sn^{4+}	Sulphides

III	$NH_4Cl + NH_4OH$	Fe^{3+}, Al^{3+}, Cr^{3+}	Hydroxides
IV	$NH_4Cl + NH_4OH + H_2S$ gas	Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}	Sulphides
V	$(NH_4)_2CO_3 + NH_4OH + NH_4Cl$	Ca^{2+}, Sr^{2+}, Ba^{2+}	Carbonates
VI	$Na_2HPO_4 + NH_4OH$	Mg^{2+}	Phosphates

Analysis of Basic Radicals : Zero group $[NH_4^+]$: To the salt, add NaOH solution and heat. If ammonia gas evolves, NH_4^+ is present.
Pass the gas through Nessler's reagent $\rightarrow$ Brown ppt. $\rightarrow$ NH_4^+ confirmed.





Detection of N, S, Cl in organic compounds

Lassaigne's extract :

A small pellet of metallic sodium together with a little amount of the substance is heated to red hot in an ignition tube. It is then suddenly plunged into about 10 mL of distilled water in a China dish. The mixture is boiled well and filtered. Filtrate is known as Lassaigne's extract (L.E.).

Element	Detection	Confirmatory test	Reactions
Nitrogen	Lassaigne's extract (L.E.) $Na + C + N \xrightarrow{\Delta} \underset{\text{(L.E.)}}{NaCN}$	L.E. + $FeSO_4$ + NaOH, boil and cool + $FeCl_3$ + conc. HCl Gives blue or green colour.	$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$ $Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$ $Na_4[Fe(CN)_6] + FeCl_3 \xrightarrow{HCl} \underset{\text{Prussian blue}}{NaFe[Fe(CN)_6]} + 3NaCl$ or $3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$

Sulphur	$2Na + S \xrightarrow{\Delta} \underset{\text{(L.E.)}}{Na_2S}$	(i) L.E. + sodium nitroprusside A deep violet colour. (ii) L.E. + CH_3COOH + $(CH_3COO)_2Pb$ Gives a black ppt.	(i) $Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Deep violet}}{Na_4[Fe(CN)_5NOS]}$ (ii) $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} \underset{\text{Black ppt.}}{PbS\downarrow} + 2CH_3COONa$
Halogens	$Na + X \xrightarrow{\Delta} \underset{\text{(L.E.)}}{NaX}$ (X = Cl, Br, I)	L.E. + HNO_3 + $AgNO_3$ (i) White ppt. soluble in aq. NH_3 (or NH_4OH) confirms Cl. (ii) Pale yellow ppt. partially soluble in aq. NH_3 (or NH_4OH) confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 (or NH_4OH) confirms I.	$NaX + AgNO_3 \xrightarrow{HNO_3} \underset{\text{White ppt.}}{AgX\downarrow} + NaNO_3$ $AgCl + 2NH_4OH_{(aq.)} \longrightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl} + 2H_2O$
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta} \underset{\text{(L.E.)}}{NaSCN}$ Sodium thiocyanate	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$3NaSCN + FeCl_3 \longrightarrow \underset{\text{Blood red colour}}{[Fe(SCN)_3]} + 3NaCl$

SPEED PRACTICE

1. An aqueous solution of 6.3 g oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is
   (a) 40 mL (b) 20 mL
   (c) 10 mL (d) 4 mL

2. Which of the following compounds does not show Lassaigne's test for nitrogen?
   (a) Urea (b) Hydrazine
   (c) Phenylhydrazine (d) Azobenzene

3. The group reagent for the group V radicals is
   (a) $(NH_4)_2CO_3$ (b) $(NH_4)_2SO_4$
   (c) NH_4Cl (d) $(NH_4)_2C_2O_4$

4. In qualitative analysis, Cd^{2+} is under
   (a) group IV (b) group III
   (c) group II (d) group I.

5. A colourless salt gives violet colour in Bunsen flame, it may be
   (a) Na_2CO_3 (b) Na_2CrO_4
   (c) K_2CO_3 (d) $BaCO_3$.

6. A doctor by mistake administered $Ba(NO_3)_2$ solution to a patient for radiography investigations. Which of the following should be given as the best to prevent the absorption of soluble barium?
   (a) Na_2CO_3 (b) NH_4Cl
   (c) NaCl (d) Na_2SO_4

7. Which of the following compounds are partially soluble or insoluble in NH_4OH solution?
   (1) $Fe(OH)_3$ (2) Ag_2CrO_4
   (3) $Al(OH)_3$ (4) Ag_2CO_3
   (5) $Ni(OH)_2$
   (a) 1, 3 (b) 2, 3, 5 (c) 1, 3, 5 (d) 2, 3, 4

8. Unknown salt 'A' + $K_2Cr_2O_7$ + conc. H_2SO_4 $\rightarrow$ Reddish brown fumes
Which is the correct statement regarding the above observation?
(a) It confirms the presence of Br^- ion.
(b) It neither confirms Cl^- nor Br^- ion unless it is passed through NaOH solution.
(c) It confirms the presence of Cl^- ion.
(d) It confirms the presence of both Cl^- and Br^- ions.

9. A pink coloured salt turns blue on heating. The presence of which cation is most likely?
(a) Cu^{2+} (b) Fe^{2+} (c) Zn^{2+} (d) Co^{2+}
(JEE Main Online 2015)

10. The difference between titrant and titrate is that
(a) titrant is a solution of an accurately known concentration whereas a titrate is the substance whose concentration is to be determined by titration
(b) titrant is a solution of unknown concentration whereas titrate is a solution of known concentration
(c) one is titrated against the other
(d) one is the reactant and the other is the product.

11. In the titration of HCl against NH_4OH, the pH at the equivalence point will be
(a) less than 7 (b) greater than 7
(c) equal to 7 (d) none of these.

12. What is the pH of the resulting solution when equal volumes of 0.1 M NaOH and 0.01 M HCl are mixed?
(a) 2.0 (b) 7.0 (c) 1.04 (d) 12.65
(NEET 2015)

13. A solution containing Na_2CO_3 and $NaHCO_3$ is titrated against HCl. The volume of the acid used when methyl orange is added as indicator is 'x' mL and the volume of the acid used when phenolphthalein is added as indicator is 'y' mL. The volume of HCl used for the neutralization of $NaHCO_3$ will be
(a) $(x - y)$ mL (b) $(x - 2y)$ mL
(c) $(x + y)$ mL (d) $(x + 2y)$ mL

14. A solution containing Na_2CO_3 and NaOH requires 300 mL of 0.1 N HCl using phenolphthalein as an indicator. Methyl orange is then added to above titrated solution when a further 25 mL of 0.2 N HCl is required. The amount of NaOH present in solution is
(a) 0.8 g (b) 1.0 g
(c) 1.5 g (d) 2 g

15. In Lassaigne's test, the organic compound is fused with a piece of sodium metal in order to
(a) increase the ionisation of the compound
(b) decrease the melting point of the compound
(c) increase the reactivity of the compound
(d) convert the covalent compound into a mixture of ionic compounds.

16. The only cations present in a slightly acidic solution are Fe^{3+}, Zn^{2+} and Cu^{2+}. The reagent that when added in excess to this solution would identify and separate Fe^{3+} in one step is
(a) 2 M HCl (b) 6 M NH_3
(c) 6 M NaOH (d) H_2S gas.

17. An aqueous solution of a salt X turns blood red on treatment with KSCN and blue on treatment with $K_4[Fe(CN)_6]$. X also gives positive chromyl chloride test. The salt X is
(a) $CuCl_2$ (b) $FeCl_3$
(c) $Cu(NO_3)_2$ (d) $Fe(NO_3)_3$
(JEE Main Online 2015)

18. Before testing for halogens, the Lassaigne's extract is boiled with
(a) conc. HCl (b) NaOH
(c) conc. HNO_3 (d) any of these.

19. A solid compound X on heating gives CO_2 gas and a residue. The residue when mixed with water forms Y. On passing an excess of CO_2 through Y in water, a clear solution Z is obtained. On boiling Z, compound X is reformed. The compound X is
(a) $Ca(HCO_3)_2$ (b) $CaCO_3$
(c) Na_2CO_3 (d) K_2CO_3

20. A salt is heated first with dil. H_2SO_4 and then with conc. H_2SO_4. No reaction takes place. It may be
(a) nitrate (b) sulphide
(c) oxalate (d) sulphate.

21. The phenomenon in which white transparent crystal changes into white powder is called
(a) efflorescence (b) allotropy
(c) sublimation (d) none of these.

22. Which of the following salts will give highest pH in water?
(a) KCl (b) NaCl
(c) Na_2CO_3 (d) $CuSO_4$ **(NEET 2014)**

23. Give the correct order of initials T or F for the following statements. Use T if statement is true and F if it is false :
(i) Cu^+ undergoes disproportionation to Cu and Cu^{2+} in aqueous solution.
(ii) $HgCl_2$ does not give chromyl chloride test.
(iii) Sulphide ions react with sodium nitroprusside to form a green coloured complex. In this reaction, oxidation state of iron changes.
(a) TFT (b) TTF (c) TFF (d) FTT

24. The presence of magnesium is confirmed in the qualitative analysis by the formation of a white crystalline precipitate of
(a) $Mg(HCO_3)_2$ (b) $MgNH_4PO_4$
(c) $MgNH_4(HCO_3)_3$ (d) $MgCO_3$

25. Match the following :

	Column-I		Column-II
P.	Presence of halogen	1.	$HNO_3/AgNO_3$
Q.	Presence of sulphur	2.	$FeCl_3$
R.	Presence of nitrogen	3.	$Na_2[Fe(CN)_5NO]$
S.	Presence of nitrogen and sulphur	4.	$FeSO_4$/dil. H_2SO_4

	P	Q	R	S
(a)	1	3	4	2
(b)	2	4	1	2
(c)	1	2	3	4
(d)	4	3	2	1

26. Cl_2 gas is continuously passed with constant shaking through Lassaigne's extract containing CS_2. If the extract contains both NaBr and NaI, first a violet colour is produced, then the organic layer turns colourless and finally orange colour is seen in the CS_2 layer. The CS_2 turns colourless between violet and orange colour due to the formation of
(a) IBr (b) ICl (c) $BrCl_3$ (d) NaI_3

27. Positive Beilstein test for halogens shows that
(a) a halogen is absent
(b) a halogen is definitely present
(c) a halogen may be present
(d) all the statements are correct.

28. The weight of oxalic acid required to neutralise 100 mL of 1 N NaOH solution, is
(a) 6.3 g (b) 126 g (c) 530 g (d) 63 g

29. In the titration of HCl against NaOH the indicator(s) used and the end point(s) obtained are
(a) phenolphthalein, pink to colourless
(b) methyl orange, yellow to red
(c) both (a) and (b) separately
(d) none of these.

30. Reddish-brown (chocolate) ppt. is formed with
(a) Cu^{2+} and $Fe(CN)_6^{4-}$ (b) Ba^{2+} and SO_4^{2-}
(c) Pb^{2+} and I^- (d) none of these.

SOLUTIONS

1. **(a) :** Normality of oxalic acid $= \dfrac{6.3 \times 1000}{63 \times 250} = 0.4$
$N_1V_{1(\text{NaOH})} = N_2V_{2\,(\text{oxalic acid})}$
$0.1 \times V_1 = 0.4 \times 10 \quad \Rightarrow \quad V_1 = 40$ mL

2. **(b) :** Hydrazine (NH_2NH_2) does not contain carbon and hence on fusion with Na metal, it cannot form NaCN, consequently hydrazine does not show Lassaigne's test for nitrogen.

3. **(a)** 4. **(c)** 5. **(c)**

6. **(d) :** $Ba(NO_3)_2$ gives precipitate of $BaSO_4$ with Na_2SO_4.

7. **(a) :** Due to insoluble nature of $Fe(OH)_3$ and $Al(OH)_3$ in NH_4OH such metals are detected in group III analysis.

8. **(b) :** When brown vapours of chromyl chloride (CrO_2Cl_2) are passed through NaOH solution it gives yellow solution of Na_2CrO_4 which confirms the presence of Cl^- ions.

9. **(d) :** In aqueous solution, Co^{2+} ion exists as $[Co(H_2O)_6]^{2+}$ ion and has pink colour. When heated, it turns blue due to dehydration.

10. **(a) :** Titrant is a solution of known concentration generally taken in the burette and titrate is the solution of the substance whose concentration is to be determined by titration.

11. **(a) :** $HCl + NH_4OH \xrightleftharpoons{\text{Neutralization}} NH_4Cl + H_2O$
$NH_4Cl + H_2O \xrightleftharpoons{\text{Hydrolysis}} NH_4OH + HCl$
Since on hydrolysis, strong acid, HCl is produced, the pH of the solution will be less than 7.

12. (d) : One mole of NaOH is completely neutralised by one mole of HCl.

Hence, 0.01 mole of NaOH will be completely neutralised by 0.01 mole of HCl.

$\Rightarrow$ NaOH left unneutralised = 0.1 – 0.01= 0.09 mol

As equal volumes of two solutions are mixed,

$$[OH]^- = \frac{0.09}{2} = 0.045 \text{ M}$$

$\Rightarrow$ pOH = –log(0.045) = 1.35

$\therefore$ pH = 14 – 1.35 = 12.65

13. (b) : Methyl orange (*M*) indicates the neutralization of both Na_2CO_3 and $NaHCO_3$ in a mixture with HCl solution and the volume used is '*x*' mL.

$$Na_2CO_3 + 2HCl \xrightarrow{M} 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \xrightarrow{M} NaCl + H_2O + CO_2$$

Phenolphthalein (*P*) indicates the neutralization of Na_2CO_3 only upto single stage, *i.e.*, upto $NaHCO_3$ stage with HCl and the volume used is '*y*' mL.

$$Na_2CO_3 + HCl \xrightarrow{P} NaHCO_3 + NaCl$$

$\therefore$ For complete neutralization of Na_2CO_3, the volume of HCl used will be '2*y*' mL. Hence, the volume of HCl used for netralization of $NaHCO_3$ only = $(x - 2y)$ mL.

14. (b) : Let *x* eq. of Na_2CO_3 and *y* eq. of NaOH be present in the solution. In presence of phenolphthalein the reactions are

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

$$\therefore \quad \frac{x}{2} + y = \frac{300 \times 0.1}{1000} = 0.03$$

In presence of methyl orange rest of Na_2CO_3 reacts

$$\frac{x}{2} = \frac{25 \times 0.2}{1000} = 0.005$$

$\therefore$ $x = 0.01$

Then weight of Na_2CO_3 = 0.01 × 53 = 0.53 g and $y = 0.03 - 0.005 = 0.025$ thus, weight of NaOH = 0.025 × 40 = 1 g

15. (d) : To convert covalent compounds into ionic compounds such as NaCN, Na_2S, Na*X*, etc.

16. (b) : When NH_3 is added to Fe^{3+}, Zn^{2+} and Cu^{2+} ions we get brown ppt. of $Fe(OH)_3$, colourless $[Zn(NH_3)_4]^{2+}$ soluble and blue $[Cu(NH_3)_4]^{2+}$ soluble complex.

$$Fe^{3+} + 3NH_3 + 3H_2O \longrightarrow Fe(OH)_3\downarrow + 3NH_4^+$$

17. (b) : Fe^{3+} radical gives blood red colour with KSCN and blue colour with $K_4[Fe(CN)_6]$. Cl^- radical gives chromyl chloride test. Thus, the salt *X* is $FeCl_3$.

18. (c) : Lassaigne's extract is boiled with HNO_3 to decompose Na_2S and NaCN which would otherwise interfere with the tests of halogens. HCl cannot be used because we cannot add Cl^- ions when we have to test for Cl in the organic compound. NaOH also cannot be used because it would precipitate $AgNO_3$ as AgOH.

19. (b) : Solid compound *X* is $CaCO_3$ which on heating gives CaO (residue) and CO_2 gas. CaO gives $Ca(OH)_2$ (*Y*) on reacting with H_2O. $Ca(OH)_2$ reacts with excess CO_2 to give a clear solution of $Ca(HCO_3)_2$ (*Z*) which on boiling gives $CaCO_3$ (*X*) again.

20. (d) : SO_4^{2-} does not react with dil. and conc. H_2SO_4.

21. (a) : Efflorescence is the loss of water of crystallisation of hydrated crystals to change into lower hydrate or anhydrous form.

22. (c) : Na_2CO_3 which is a salt of NaOH (strong base) and H_2CO_3 (weak acid) will produce a basic solution with pH greater than 7.

23. (b)

24. (b) : $MgCl_2 + Na_2HPO_4 + NH_4OH \rightarrow$

$$\underset{\text{White ppt.}}{Mg(NH_4)PO_4} + 2NaCl + H_2O$$

25. (a)

26. (b) : I_2 first liberated combines with Cl_2 to form colourless iodine monochloride.

$$I_2 + Cl_2 \longrightarrow 2ICl$$

27. (c) : Positive Beilstein test does not necessarily mean that halogen is definitely present because certain compounds such as urea, thiourea, pyridine, etc. which do not contain halogen, also give this test. Therefore, positive Beilstein test shows that halogen may be present.

28. (a) : Number of eq. of NaOH = Number of eq. of oxalic acid

$$\therefore \quad \frac{100 \times 1}{1000} = \frac{\text{Wt. of oxalic acid}}{63}$$

Weight of oxalic acid = 6.3 g

29. (c) : In the titration of strong acid vs strong base, both the indicators phenolphthalein (pink to colourless) and methyl orange (yellow to red) can be used separately.

30. (a) : $Cu_2[Fe(CN)_6]$ is chocolate brown colour precipitate.

NEET | JEE ESSENTIALS

Class XII

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Unit 9 Principles Related to Practical Chemistry

SURFACE CHEMISTRY

Preparation of Lyophilic Sol

- **Starch sol :** Starch is an intrinsic colloid, forms a hydrophilic sol directly when mixed with hot water. It is quite stable as it is electrically neutral.
- **Gum-arabic :** Gum-arabic is hydrophilic colloid and therefore, readily forms sol on shaking with water. The sol is stable as it is not affected by ionic impurities.
- **Egg albumin :** Egg albumin forms hydrophilic sol with water at room temperature. It is quite stable and not affected by the presence of any impurity.

Preparation of Lyophobic Sol

- **Hydrated ferric oxide sol :** It is prepared indirectly by the hydrolysis of ferric chloride with boiling water. Ferric ions produced from $FeCl_3$ solution are adsorbed on the surface of the particles of $Fe(OH)_3$.

$$FeCl_{3(aq)} + 3H_2O_{(l)} \xrightarrow{\Delta} \underset{\text{Red sol}}{Fe(OH)_{3(s)}} + 3HCl_{(aq)}$$

- **Hydrated aluminium oxide sol :** It is prepared by hydrolysis of aluminium chloride.

$$AlCl_{3(aq)} + 3H_2O_{(l)} \xrightarrow{\Delta} \underset{\text{White sol}}{Al(OH)_{3(s)}} + 3HCl_{(aq)}$$

- **Arsenious sulphide sol :** It is prepared by passing hydrogen sulphide gas through a dilute aqueous solution of arsenious oxide.

$$As_2O_{3(aq)} + 3H_2S_{(g)} \longrightarrow \underset{\text{Yellow sol}}{As_2S_{3(s)}} + 3H_2O_{(l)}$$

CHEMICAL KINETICS

Rate of Decomposition of H_2O_2 :

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

The reaction is catalysed by iodide ions.

$$H_2O_2 + I^- \xrightarrow{\text{Slow}} H_2O + \underset{\text{Hypoiodite ion}}{IO^-}$$

$$IO^- + IO^- \xrightarrow{\text{Fast}} 2I^- + O_2$$

or $H_2O_2 + IO^- \xrightarrow{\text{Fast}} H_2O + I^- + O_2$

Thus, rate law equation is

$$\text{Rate} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k'[H_2O_2][I^-]$$

If concentration of I^- ions remains constant, then the rate law equation is

$$\text{Rate} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k[H_2O_2] \qquad (\because k'[I^-] = k)$$

i.e., it is a first order reaction.

Reaction of Iodide Ion with H_2O_2 at Room Temperature :

Here, reactions involved are

- **Main reaction :**

$$H_2O_2 + 2I^- + 2H^+ \xrightarrow{\text{Slow}} I_2 + 2H_2O$$

- **Monitor reaction :**

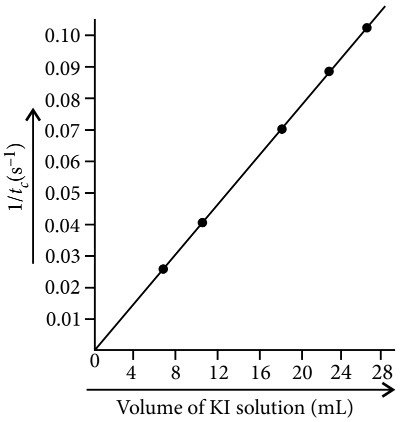
  $I_2 + 2S_2O_3^{2-} \xrightarrow{\text{Fast}} S_4O_6^{2-} + 2I^-$
- **Indicator reaction :**

  $I_2 + \text{Starch} \longrightarrow \text{Blue colour complex}$
- As the concentration of thiosulphate ion is kept constant, the different time taken (t_c) for the appearance of blue colour with change in concentration of either reactant indicates the relative rate of reaction.

  Initial rate $\propto \dfrac{1}{t_c}$

  The rate of reaction decreases with decrease in the concentration of KI.

  The graph of $1/t_c$ versus volume of KI solution is a straight line.



  Rate of reaction $\propto$ Concentration of KI

  Similarly, by keeping I^- ion concentration constant and taking different concentrations of H_2O_2, the rate *w.r.t.* H_2O_2 can be found out.

Thermochemistry

Enthalpy of Dissolution of Copper Sulphate

It is the amount of heat absorbed or evolved on dissolving one mole of substance in excess of solvent at a given temperature and pressure. It is +ve when heat is absorbed and –ve when heat is given out during dissolution.

For copper sulphate :

$CuSO_4.7H_2O_{(s)} + H_2O_{(l)} \longrightarrow CuSO_{4(aq)} + \Delta H; \Delta H = ?$

Heat gained or lost (Q) = Mass (m) × specific heat of the solution (s) × change in temperature (Δt)

Heat of the dissolution

$$= \frac{Q \times \text{Molecular weight of compound}}{\text{Weight of compound dissolved}}$$

Enthalpy of Neutralisation for a Strong Acid and a Strong Base

Heat of neutralisation is the heat evolved, when one mole of H^+ ions is completely neutralised by a base. The neutralisation reaction in case of HCl and NaOH is in accordance with Arrhenius theory of ionisation, can be written as

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$
$$H^+{}_{(aq)} + OH^-{}_{(aq)} \longrightarrow H_2O_{(l)} + 57.3 \text{ kJ}$$

Thus, the reaction between HCl and NaOH solution is, in fact, the reaction between $H^+_{(aq)}$ and $OH^-_{(aq)}$, therefore, the heat of neutralisation will be same for neutralisation of all strong acids with strong bases.

Electrochemistry

Variation of Cell Potential in Zn|Zn^{2+}|| Cu^{2+}|Cu with Change in Concentration of Electrolytes ($CuSO_4$ and $ZnSO_4$) at Room Temperature

Reduction potential of an electrode increases with increase in concentration of the electrolyte.

$$M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$$

In the zinc-copper electrochemical cell, zinc electrode acts as anode while copper electrode acts as cathode.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

E°_{cell} increases if E°_{cathode} increases and E°_{anode} decreases. Thus, higher conc. of Cu^{2+} and lower conc. of Zn^{2+} ions increase the E°_{cell} for Zn | Zn^{2+} || Cu^{2+} | Cu.

The relation between conc. of the eletrolyte and the standard electrode potential is given in the form of Nernst equation :

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

INFO SHOTS

Every therapeutic drug has a narrow range of optimal water content, which needs to be controlled to avoid potential adverse effect on patients. Recently, chemists have invented a method to quantify water content in solid pharmaceutical drugs that is faster, cheaper, more accurate and more precise than Karl Fischer titration method. In this method, water determination is done using ionic liquids and headspace gas chromatography.

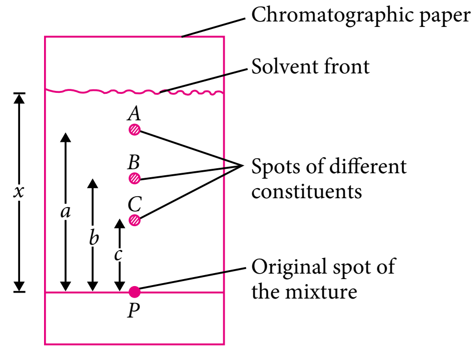
Chromatography

Chromatography is a modern and sensitive technique used for rapid and efficient analysis and separation of components of a mixture and purification of compounds.

Principle : This technique is based on the differential migration of individual components of a mixture through a stationary phase under the influence of moving phase.

The components of the mixture rise up at different rates and thus, get separated from one another and then the R_f value is calculated using the given formula :

$$R_f = \frac{\text{Distance travelled by the solute from the original line}}{\text{Distance travelled by the solvent from the original line}}$$

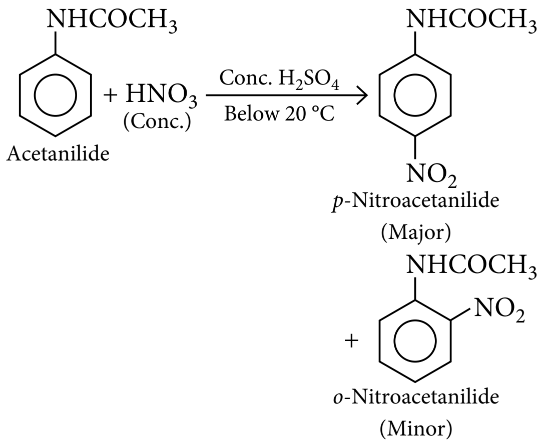


R_f value for $A = \frac{a}{x}$, for $B = \frac{b}{x}$ and for $C = \frac{c}{x}$

Preparation of Organic Compounds

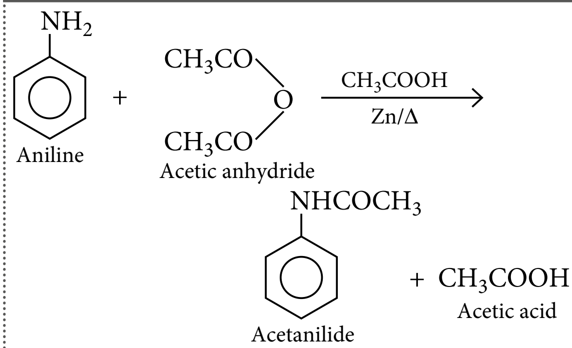
p-Nitroacetanilide

p-Nitroacetanilide is prepared by nitration of acetanilide with a mixture of conc. HNO_3 and conc. H_2SO_4 (nitrating mixture).



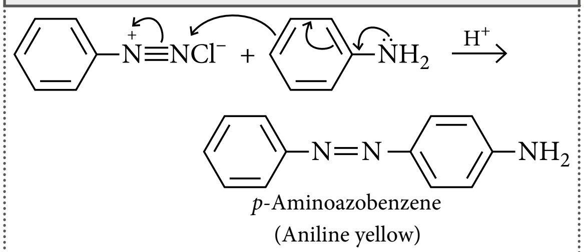
Acetanilide

It is prepared by acetylation of aniline with acetic anhydride in presence of glacial acetic acid and a small amount of zinc dust.



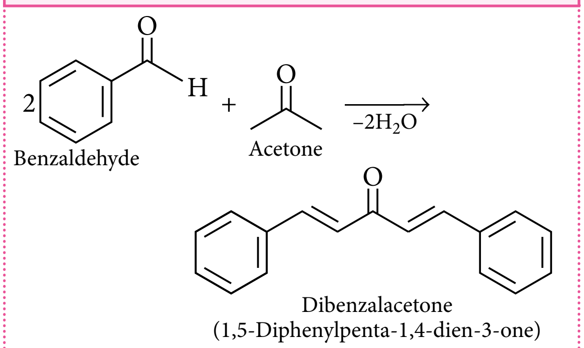
Aniline yellow

It is an azo dye, prepared by coupling benzenediazonium chloride with aniline in acidic medium.



Dibenzalacetone

Dibenzalacetone is prepared by aldol condensation of acetone with two equivalents of benzaldehyde. It is a base catalysed aldol condensation.



Detection of Functional Groups

Test for Unsaturation

Bromine test :

$$>C=C< + Br_2 \longrightarrow >CBr-CBr<$$
Alkene (sample); Br_2 (Orange red); Dibromoalkane (Colourless)

$$-C\equiv C- + 2Br_2 \longrightarrow -CBr_2-CBr_2-$$
Alkyne; Br_2 (Orange red); Tetrabromoalkane (Colourless)

Baeyer's test or Permanganate test :

$$3CH_2=CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 2KOH + 2MnO_2 + 3CH_2OH.CH_2OH$$
Ethene; $KMnO_4$ (Pink); MnO_2 (Brown); Glycol (Colourless)

$$CH\equiv CH + 2KMnO_4 + 2H_2O \longrightarrow 2KOH + 2MnO_2 + (COOH)_2$$
Ethyne; $KMnO_4$ (Pink); MnO_2 (Brown); Oxalic acid (Colourless)

Test for Alcoholic (–OH) Group

- **Sodium metal test :**

  $$ROH_{(l)} + Na_{(s)} \longrightarrow RONa + 1/2H_{2(g)}\uparrow$$
  Ethanol (sample); Sodium; Sodium ethoxide; Hydrogen (effervescence)

- **Ceric ammonium nitrate test :**

  $$2ROH + (NH_4)_2[Ce(NO_3)_6] \longrightarrow (ROH)_2Ce(NO_3)_4 + 2NH_4NO_3$$
  Colourless (sample); Ceric ammonium nitrate (yellow); (Pink or purple); (Colourless)

- **Ester test :**

  $$ROH + CH_3COOH \xrightarrow{\text{Conc. } H_2SO_4} CH_3COOR + H_2O$$
  Ethanol (sample); Acetic acid; Ethyl acetate (fruity smell); Water

- **Acetyl chloride test :**

  $$R-OH + CH_3COCl \longrightarrow CH_3COOR + HCl\uparrow$$
  Alcohol (sample); Acetyl chloride; Ester

  $$HCl\uparrow + NH_4OH \longrightarrow NH_4Cl\uparrow + H_2O$$
  White dense fumes

- **Xanthate test :**

  $$ROH + KOH \xrightarrow[\text{(ii) Cool (iii) Ether}]{\text{(i) }\Delta} ROK + H_2O$$
  Alcohol (Sample)

  $$ROK + CS_2 \longrightarrow RO-C(=S)S^-K^+$$
  Yellow ppt.

- **Distinction between 1°, 2° and 3° alcohols :**
  Organic compound + Lucas reagent (Anhy. $ZnCl_2$ + conc. HCl) and shake :
  – Separation of an insoluble layer at once confirms 3° alcohol.
  – Appearance of cloudiness within 4-5 minutes confirms 2° alcohol.
  – Clear solution confirms 1° alcohol.

Test for Phenolic Group

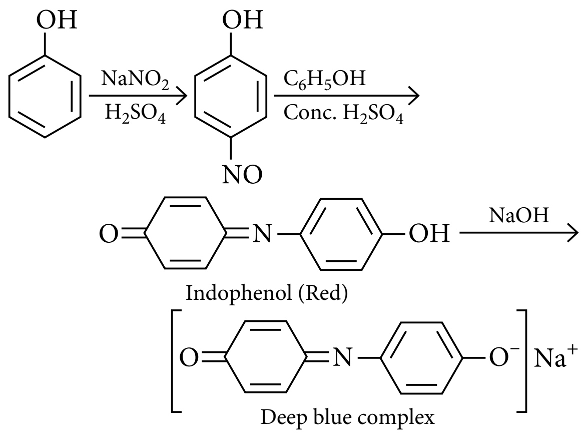
- **Ferric chloride test :**

  $$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(C_6H_5O)_6]^{3-} + 3HCl$$
  Phenol (sample); (Neutral); (Green/Red/Violet colour)

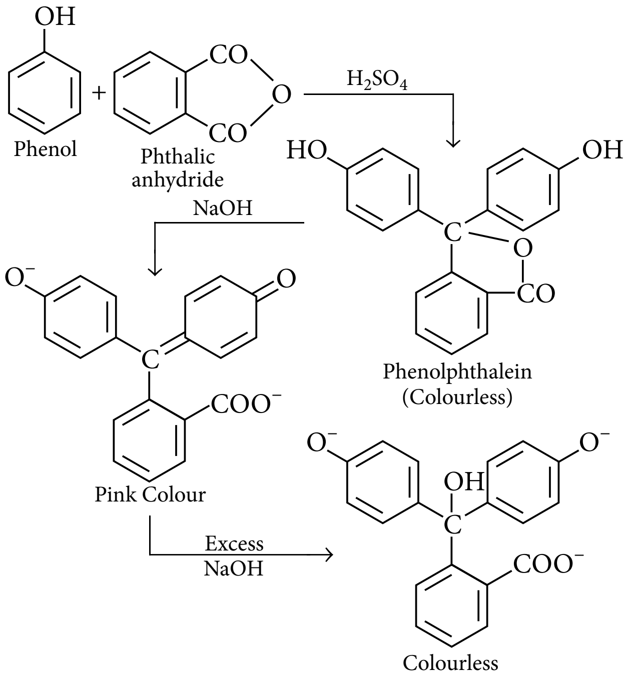
- **Litmus test :** Sample solution + Blue litmus $\longrightarrow$ Red colour

- **Br_2-water test :**
  Gives white ppt. of 2,4,6-Tribromophenol.

- **Liebermann's test :**



- **Phthalein test :**



Tests for Carbonyl ($>C=O$) group

For Ketones only

Sodium Nitroprusside Test

Sodium nitroprusside solution + NaOH + $RCOR$ $\rightarrow$ Appearance of wine-red colour.

Idoform Test (for methyl ketones)

$$R{-}CO{-}CH_3 + 3I_2 + 4NaOH \rightarrow 3NaI + \underset{\substack{\text{Iodoform}\\\text{(Yellow ppt.)}}}{CHI_3\downarrow} + RCOONa + 3H_2O$$

For Aldehydes only

Schiff's Test

$$\underset{\text{(Sample)}}{RCHO} + \text{Schiff's reagent} \rightarrow \text{Deep red/violet colour}$$

Tollens' Test

$$\underset{\text{(Sample)}}{RCHO} + \underset{\text{Tollens' reagent}}{2[Ag(NH_3)_2]OH} \rightarrow \underset{\substack{\text{Silver}\\\text{mirror}}}{2Ag\downarrow} + RCOONH_4 + 3NH_3 + H_2O$$

Fehling Solution Test

$$RCHO + \underset{\substack{\text{(Fehling}\\\text{solution}\\(A+B))}}{2CuO} \rightarrow \underset{\text{Red ppt.}}{Cu_2O\downarrow} + RCOOH$$

Benedict's Test

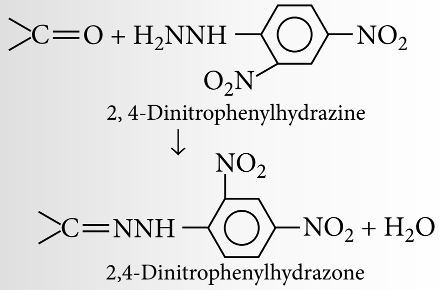
$$\underset{\text{Sample}}{RCHO} + \underset{\substack{\text{Benedict solution}\\\text{(Blue)}}}{2Cu(OH)_2} + NaOH \rightarrow RCOONa + \underset{\text{Red ppt.}}{Cu_2O\downarrow} + 3H_2O$$

For both Aldehydes and Ketones

Sodium Bisulphite Test

$$\underset{\text{Sample}}{>C=O} + NaHSO_3 \rightarrow \underset{\text{(White ppt.)}}{>C(OH)SO_3^-Na^+}$$

2, 4-DNP Test (Brady's reagent test)



2, 4-Dinitrophenylhydrazine

2,4-Dinitrophenylhydrazone (Orange/red ppt.)

Tests for Amino ($-NH_2$) group

Carbylamine Test :

$$\underset{\text{(Sample)}}{RNH_2} + CHCl_3 + 3KOH \rightarrow \underset{\substack{\text{Carbylamine}\\\text{(Offensive odour)}}}{RNC\uparrow} + 3KCl + 3H_2O$$

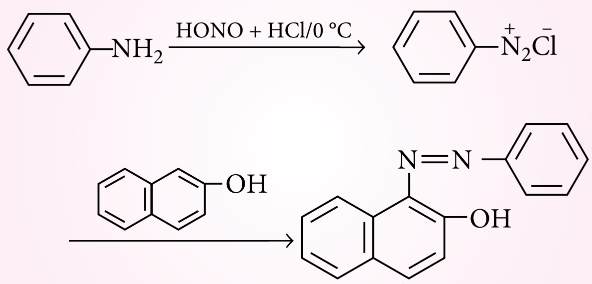
Nitrous Acid Test :

$$\underset{1^\circ\text{ Amine}}{RNH_2} + HNO_2 \longrightarrow ROH + H_2O + \underset{\substack{\text{Brisk}\\\text{Effervescence}}}{N_2\uparrow}$$

$$\underset{2^\circ\text{ Amine}}{R_2NH} + HONO \longrightarrow \underset{\substack{\text{Nitrosoamine,}\\\text{(Yellow oil)}}}{R_2N \rightarrow NO} + H_2O$$

$$\underset{3^\circ\text{ Amine}}{R_3N} + HONO \longrightarrow \underset{\substack{\text{Trialkyl ammonium}\\\text{nitrate}}}{R_3N^+HONO^-}$$

Azo-dye Test : (For Aromatic 1°Amine)



Orange/red ppt.
(2-Naphthol aniline dye)

Distinction between 1°, 2° and 3° Amine (Hinsberg's Test)

Amine + NaOH + Benzene Sulphonyl Chloride

- Ppt. formed $\xrightarrow{\text{Conc. HCl}}$
  - Ppt. dissolved (3° Amine present)
  - Ppt. insoluble (2° Amine present)
- Clear solution $\xrightarrow{\text{Conc. HCl}}$ Insoluble mass formed (1° Amine)

Test for Carboxylic (—COOH) Group

- **Sodium bicarbonate test :**

$$\underset{\text{(Sample)}}{RCOOH} + NaHCO_3 \longrightarrow RCOONa + H_2O + \underset{\text{(Effervescence)}}{CO_2\uparrow}$$

- **Litmus test :**

$$\underset{\text{(Sample)}}{RCOOH} + \text{Blue litmus} \longrightarrow \text{Red}$$

Note : Phenols also give this test.

- **Ester test :**

$$RCOOH + C_2H_5OH \xrightarrow[\Delta]{\text{conc. } H_2SO_4} \underset{\substack{\text{Ester}\\ \text{(Fruity smell)}}}{RCOOC_2H_5} + H_2O$$

Characteristic Tests for Carbohydrates, Fats and Proteins

- **Tests for carbohydrates :**

Tests for carbohydrates

- Simple carbohydrates ↓ Monosaccharides or disaccharides + Benedict's solution (Blue coloured) ↓ Changes to orange red or brick red
- Complex sugar ↓ Starch + I_2 solution (Lugol's reagent) (Yellowish-brown) ↓ Changes to dark purple/black

- **Tests for lipids :**
  - **Grease spot test :** Lipid leaves translucent spot on unglazed brown paper bags.
  - **Sudan red test :** Sudan red is a fat soluble dye that stains lipids red.

- **Test for proteins :**
  - **Biuret test :**

$$\begin{matrix}\text{Biuret solution}\\ \text{(Blue) + Sample}\end{matrix} \longrightarrow \begin{matrix}\text{Purple or}\\ \text{pink solution}\end{matrix} \begin{pmatrix}\text{For peptides with}\\ \text{chain length of at}\\ \text{least 3-amino acids}\end{pmatrix}$$

Volumetric Analysis

- In a titration, a volume of a standardized solution containing a known concentration of reactant '*A*' is added incrementally to a sample containing an unknown concentration of reactant '*B*' till reactant '*B*' is just consumed (stoichiometric completion). This is known as the equivalence point.
  At this point we have, $N_1V_1 = N_2V_2$.
- Strength = Normality × Equivalent weight
  Relation between normality and molarity :
  Normality = n × Molarity
  where, n = number of equivalents in 1 mole.

Titration of Oxalic Acid with $KMnO_4$

- $2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$$5\begin{matrix}COOH\\ |\\ COOH\end{matrix} + 5[O] \longrightarrow 5H_2O + 10CO_2\uparrow$$

- **Indicator :** $KMnO_4$ is self indicator.
- **End point :** Appearance of light pink colour.
- **Observations :**

S.No.	Initial burette reading (R_1)	Final burette reading (R_2)	Volume of $KMnO_4$ used $V_1 = (R_2 - R_1)$
1			
2			

- **Calculation :** $\underset{(KMnO_4)}{n_1 \times M_1 \times V_1} = \underset{\text{(Oxalic acid)}}{n_2 \times M_2 \times V_2}$

Molarity of $KMnO_4$ $(M_1) = \dfrac{n_2 \times M_2 \times V_2}{n_1 \times V_1}$

where, $n_1 = 5$ and $n_2 = 2$

Titration of Mohr's Salt vs $KMnO_4$

- $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + 68H_2O$
- **Indicator :** $KMnO_4$ is self indicator.
- **End Point :** Appearance of light pink colour.
- **Observation :**

S.No.	Initial burette reading (R_1)	Final burette reading (R_2)	Volume of $KMnO_4$ used $V_1 = (R_2 - R_1)$
1			
2			

- **Calculation :** $\underset{(KMnO_4)}{n_1 \times M_1 \times V_1} = \underset{(\text{Mohr's salt})}{n_2 \times M_2 \times V_2}$

Molarity of $KMnO_4 (M_1) = \dfrac{n_2 \times M_2 \times V_2}{n_1 \times V_1}$

where, $n_1 = 5$ and $n_2 = 1$

Preparation of Inorganic Compounds

Ferrous Ammonium Sulphate (Mohr's Salt)

It is a double salt, prepared by dissolving equimolar quantities of iron(II) sulphate and ammonium sulphate in water containing a little amount of sulphuric acid, and then subjecting the resulting solution to crystallization.

$$\underset{(1\text{ mole, }278\text{ g})}{FeSO_4.7H_2O} + \underset{(1\text{ mole, }132\text{ g})}{(NH_4)_2SO_4} \longrightarrow \underset{(1\text{ mole, }392\text{ g})}{FeSO_4.(NH_4)_2SO_4.6H_2O} + H_2O$$

Potash alum (*Phitkari*)

It is a double salt of potassium sulphate and aluminium sulphate prepared by concentrating a solution containing equimolar quantities of K_2SO_4 and $Al_2(SO_4)_3.18H_2O$ to crystallization point followed by cooling.

$$\underset{(1\text{ mole, }174\text{ g})}{K_2SO_4} + \underset{(1\text{ mole, }666\text{ g})}{Al_2(SO_4)_3.18H_2O} + 6H_2O \longrightarrow \underset{(1\text{ mole, }948\text{ g})}{K_2SO_4.Al_2(SO_4)_3.24H_2O}$$

SPEED PRACTICE

1. Liebermann's test is used for identification of which functional group in organic compounds?
(a) Alcohol
(b) 1° Amine
(c) Phenolic
(d) Aldehyde

2. Which of the following statements is not correct regarding preparation of *p*-nitroacetanilide?
(a) Nitration of acetanilide gives a mixture of *o*- and *p*-nitroacetanilide in which *p*-isomer predominates.
(b) Nitration is carried out with a mixture of conc. HNO_3 + conc. H_2SO_4
(c) During crystallisation of the crude product, *p*-nitroacetanilide crystallises out leaving *o*-nitroacetanilide in the mother liquor.
(d) *o*-Nitroacetanilide is colourless but *p*-nitroacetanilide is yellow coloured

3. The purpose of adding dilute sulphuric acid in the preparation of Mohr's salt is to
(a) prevent the hydrolysis of ferrous sulphate
(b) increase the solubility of the salts used
(c) prevent the precipitation of carbonates of metals
(d) neutralize ammonium salts.

4. Some pale green crystals are strongly heated. The gases given off are passed into a container surrounded by ice and then through a solution of acidified $KMnO_4$. $KMnO_4$ is decolourised and a waxy white solid is formed in the ice container, this is dissolved in water. The solution will
(a) give a precipitate with silver nitrate solution
(b) give a precipitate with barium chloride solution
(c) turn red litmus blue
(d) give blue colour with starch solution.

5. Experiments on the oxidation of I^- ions by H_2O_2 in presence of dilute H_2SO_4, $S_2O_3^{2-}$ ions and starch were repeated, taking the same amount of 3% H_2O_2 but varying amounts of 0.5 M KI solution (*e.g.*, 20 mL, 16 mL, 12 mL etc. and making the volume to 20 mL in each case by adding water). The time for the appearance of blue colour was noted. Then
(a) a plot of volume of KI solution *vs* time will be linear
(b) a plot of volume of KI solution *vs* 1/time will be linear
(c) a plot of 1/volume of KI solution *vs* 1/time will be linear
(d) there is no relationship between volume of KI solution and time.

6. A solution containing a group IV cation gives a precipitate on passing H_2S gas. A solution of this precipitate in dil. HCl produces a white precipitate with NaOH solution and bluish white precipitate with basic potassium ferrocyanide. The cation is
(a) Co^{2+} (b) Ni^{2+} (c) Zn^{2+} (d) Mn^{2+}.

(JEE Main Online 2017)

7. 3.92 g of ferrous ammonium sulphate reacts completely with 50 mL of $\frac{N}{10}$ $KMnO_4$ solution. The percentage purity of the sample is
(a) 50 (b) 78.4 (c) 80 (d) 39.2.

8. A metal chloride dissolves appreciably in cold water and when placed on a platinum wire in Bunsen flame, no distinctive colour is noticed, the cation would be
(a) Mg^{2+} (b) Ba^{2+} (c) Pb^{2+} (d) Ca^{2+}.

9. A white crystalline solid *A*, on boiling with caustic soda solution gave a gas *B* which when passed through an alkaline solution of potassium mercuric iodide gave a brown ppt. The substance *A* on heating gave a gas *C* which rekindled a glowing splinter but did not give brown fumes with nitric oxide. The gases *B*, *C* and the substance *A* respectively are
(a) H_2S, NO_2 and NaCl
(b) NH_3, N_2O and NH_4NO_3
(c) HCl, NO and NH_4Cl
(d) CO_2, SO_2 and Na_2SO_3.

10. Match the list-I with list-II and choose the correct option using the codes given below :

List - I (Functional group)		**List - II (Reagent)**
P.	$-OH$	(i) Ceric ammonium nitrate
Q.	$-COOH$	(ii) 2, 4-DNP
R.	$>C=O$	(iii) $NaHCO_3$
S.	$-NH_2$	(iv) $C_6H_5SO_2Cl$

	P	**Q**	**R**	**S**
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iv)	(iii)	(ii)	(i)
(c)	(i)	(ii)	(iv)	(ii)
(d)	(i)	(iii)	(ii)	(iv)

11. Dimethylglyoxime (DMG) gives a red precipitate with Ni^{2+}, which is used for its detection. To get this precipitate, the best pH range is
(a) < 1 (b) 2 - 3 (c) 3 - 4 (d) 9 - 11

12. The pair(s) of ions where both the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is(are)
(a) Ba^{2+}, Zn^{2+} (b) Bi^{3+}, Fe^{3+}
(c) Cu^{2+}, Pb^{2+} (d) Hg^{2+}, Bi^{3+}

(JEE Advanced 2015)

13. The brown ring test for NO_2^- and NO_3^- ions is due to the formation of complex ion with formula,
(a) $[Fe(H_2O)_6]^{2+}$ (b) $[Fe(NO)(CN)_5]^{2-}$
(c) $[Fe(H_2O)_5(NO)]^{2+}$ (d) $[Fe(H_2O)(NO)_5]^{2+}$

14.
$$\begin{array}{ccccc} \text{(Clear solution) } B & \xleftarrow{\text{dil. HCl}} & A & \xrightarrow{K_2CrO_4} & D \text{ (Yellow ppt.)} \\ & & \downarrow{\scriptstyle \text{dil.} H_2SO_4} & & \\ & & C \text{ (White ppt.)} & & \end{array}$$

Compound *A* is
(a) barium carbonate (b) calcium carbonate
(c) lead carbonate (d) red lead.

15. $KMnO_4$ reacts with oxalic acid according to the equation,
$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$
Here 20 mL of 0.1 M $KMnO_4$ is equivalent to

(a) 50 mL of 0.5 M $C_2H_2O_4$
(b) 20 mL of 0.1 M $C_2H_2O_4$
(c) 20 mL of 0.5 M $C_2H_2O_4$
(d) 50 mL of 0.1 M $C_2H_2O_4$.

16. An organic compound produces effervescence with $NaHCO_3$ solution. It dissolves in NaOH solution and gets precipitated when dil. HCl is added to it. The compound is
(a) acetic acid (b) benzoic acid
(c) oxalic acid (d) formic acid.

17. Leveling bulb is used during experiment to study kinetics of dissociation of hydrogen peroxide to ensure
(a) pressure within the reaction vessel is same as that in the room
(b) uniform pressure difference between the room and the gases in the system
(c) same temperature as that of room
(d) none of these.

18. Gold sol has been prepared by shaking gold chloride ($AuCl_3$) solution with formaldehyde. Which one of the following is true?
(a) $AuCl_3$ has been oxidised by formaldehyde.
(b) $AuCl_3$ has been reduced by formaldehyde.
(c) $AuCl_3$ has been reduced as well as oxidised, *i.e.*, it is a disproportionation reaction.
(d) Reaction between $AuCl_3$ and HCHO is a displacement reaction.

19. Which of the following statements is incorrect?
(I) In $S_2O_3^{2-}$, both sulphur are different in nature.
(II) Sodium acetate and lead acetate on heating give same type of products, whereas Mn, Sn, Fe oxalate salts give different types of products.
(III) Aqueous solution of OCl^-, S^{2-} and CO_3^{2-} ions is basic in nature.
(IV) NO_2^- oxidises I^- ion whereas Br_2 and Cl_2 oxidises NO_2^- ions.
(a) II, IV only (b) I, II, IV only
(c) II only (d) II, III, IV only

20. Which of the following compounds is responsible for yellow colour in the xanthate test for alcoholic group?
(a) $RO-\overset{\overset{\large O}{\|}}{C}-O^-K^+$ (b) $RO-\overset{\overset{\large S}{\|}}{C}-S^-K^+$
(c) $RO-\overset{\overset{\large S}{\|}}{C}-SR$ (d) $RO-\overset{\overset{\large S}{\|}}{C}-OR$

21. The cation that will not be precipitated by H_2S in the presence of dil. HCl is
(a) Cu^{2+} (b) Pb^{2+} (c) As^{3+} (d) Co^{2+}
(JEE Main Online 2015)

22. To determine the enthalpy of neutralization of HCl with NaOH, we use
(a) 0.2 N HCl and 0.2 N NaOH
(b) 0.5 N HCl and 0.5 N NaOH
(c) 1 N HCl and 1 N NaOH
(d) any of these.

23. Sometimes a brown precipitate of hydrated MnO_2 ($MnO_2.H_2O$) is observed in $KMnO_4$ titrations. This is due to
(a) insufficient quantity of dil. H_2SO_4 which results in incomplete reduction of $KMnO_4$
(b) over heating of the solution
(c) dropwise addition of $KMnO_4$ with constant shaking
(d) addition of hydrochloric acid.

24. In the preparation of *p*-nitroacetanilide from aniline, nitration is not done by using nitrating mixture (a mixture of conc. H_2SO_4 and conc. HNO_3) because

(a) it gives *o*-nitroacetanilide
(b) it gives a mixture of *o*- and *p*-nitroaniline
(c) $-NH_2$ group gets oxidised
(d) it forms a mixture of *o*-and *p*-nitroacetanilide.

25. Few drops of HNO_3 are added before proceeding for group III in order to
(a) convert Fe^{2+} to Fe^{3+}
(b) convert Fe^{3+} to Fe^{2+}
(c) precipitate group III radicals
(d) none of these.

26. A known coloured solution containing two metal ions, was treated with excess cold sodium hydroxide solution. When filtered a whitish solid, slowly changing to brown, was retained on the filter paper and a colourless solution collected as the filtrate. Dropwise addition of hydrochloric acid to the filtrate produced a white ppt. which dissolved in excess acid. Treatment of the residue on filter paper with a solution of strong oxidiser produced a reddish-violet solution. Indicate the pairs of ions.
(a) Mn^{2+} and Mg^{2+} ions
(b) Fe^{2+} and Zn^{2+} ions
(c) Zn^{2+} and Mn^{2+} ions
(d) Mg^{2+} and Zn^{2+} ions

27. A solution of metal hydroxide (*M*OH) with copper sulphate and mixed tartarate of metal *M* with another metal M_1 of the same group, is used in the detection of —CHO group. Metal *M* and M_1 are respectively
(a) Na, Li (b) Rb, Na (c) K, Na (d) K, Rb

28. In the electrochemical cell :
$Zn|ZnSO_4(0.01\ M)||CuSO_4(1.0\ M)|Cu$, the emf of this Daniell cell is E_1. When the concentration of $ZnSO_4$ is changed to 1.0 M and that of $CuSO_4$ changed to 0.01 M, the emf changes to E_2. Which one is the correct relationship between E_1 and E_2? (Given, $RT/F = 0.059$)
(a) $E_1 < E_2$ (b) $E_1 > E_2$
(c) $E_2 = 0\ E_1$ (d) $E_1 = E_2$
(NEET 2017)

29. Ferric hydroxide sol can be prepared
(a) by shaking $FeCl_3$ solution with dilute NaOH solution
(b) by shaking freshly precipitated $FeCl_3$ with cold water
(c) by shaking freshly precipitated $Fe(OH)_3$ with water
(d) by shaking $FeCl_3$ with boiling water.

30. The sol of egg albumin is prepared by shaking
(a) the white of the egg with cold water
(b) the yellow of the egg with cold water
(c) the white of the egg with hot water
(d) yellow of the egg with hot water.

SOLUTIONS

1. **(c)**

2. **(d) :** *o*-Nitroacetanilide is yellow coloured while *p*-nitroacetanilide is colourless.

3. **(a) :** $FeSO_4$ undergoes hydrolysis to produce $Fe(OH)_2$ and H_2SO_4.
$FeSO_4 + 2H_2O \rightarrow Fe(OH)_2 + H_2SO_4$
To prevent hydrolysis, dil. H_2SO_4 is added in the preparation of Mohr's salt.

4. **(b) :** The salt can be $FeSO_4.7H_2O$ which produces SO_2. SO_2 decolourises $KMnO_4$ and gets oxidised to SO_3 which dissolves in water to give H_2SO_4 which gives white ppt. of $BaSO_4$ with $BaCl_2$ solution.

5. **(b) :** Volume of KI solution represents concentration and 1/time represents rate of reaction.
As rate of reaction $\propto$ concentration of KI solution, hence a plot of volume of KI solution versus 1/time will be linear.

6. **(c) :** $Zn^{2+} + H_2S \longrightarrow \underset{\text{ppt}}{ZnS} \xrightarrow{\text{dil.HCl}} ZnCl_2$

$$\underset{\text{(White ppt.)}}{Zn(OH)_2} \xleftarrow{\text{NaOH}} ZnCl_2 \xrightarrow{K_4[Fe(CN)_6]} \underset{\text{(Bluish white ppt.)}}{Zn_2[Fe(CN)_6]}$$

7. **(a) :** Normality $= \dfrac{w}{M \times V} = \dfrac{3.92}{392 \times 1} = 0.01$ N
Let % purity be *x*.
then, $N_1V_1 = N_2V_2$

$$\frac{x}{100}(0.01 \times 1000) = \left(\frac{1}{10} \times 50\right)$$

$$\left(\frac{x}{100} \text{ is the factor of purity}\right)$$

$$x = \frac{100 \times 50 \times 0.1}{0.01 \times 1000} = 50\%$$

8. **(a) :** $MgCl_2$ is soluble in cold water and does not give flame test.

9. **(b) :** Substance *A* is NH_4NO_3 which on boiling with NaOH gives NH_3 (gas *B*)

$$\underset{(A)}{NH_4NO_3} + NaOH \rightarrow NaNO_3 + \underset{(B)}{NH_3} + H_2O$$

NH_3 gives brown ppt. with Nessler's reagent (K_2HgI_4)

$$2K_2[HgI_4] + NH_3 + 3KOH \rightarrow \underset{\text{Brown ppt.}}{H_2NHgO.HgI} + 7KI + 2H_2O$$

$$\underset{(A)}{NH_4NO_3} \xrightarrow{\Delta} \underset{(C)}{N_2O} + 2H_2O$$

10. (d)

11. (d): At pH 9-11, dimethylglyoxime forms a red precipitate with Ni^{2+} as Ni-DMG complex.

12. (c, d) : Group II radicals will get precipitated out upon passing H_2S gas in presence of dilute HCl. CuS, PbS, HgS and Bi_2S_3 give black precipitates with dil. HCl.

13. (c)

14. (a): *A* is $BaCO_3$ which gives clear solution by reacting with dil. HCl but gives white ppt. of $BaSO_4$ with dil. H_2SO_4 while yellow ppt. of $BaCrO_4$ with K_2CrO_4 solution.

15. (d): $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

$\therefore$ 2 moles of $MnO_4^- \equiv$ 5 moles of $C_2O_4^{2-}$

20 mL of 0.1 M $KMnO_4$ = 2 mmol of $KMnO_4$

Also, 50 mL of 0.1 M $C_2H_2O_4$ = 5 mmol of $C_2O_4^{2-}$

Therefore, these are equivalent.

16. (b): Since the compound dissolves in NaOH and gets precipitated on addition of HCl, therefore, it must be benzoic acid.

17. (a)

18. (b): $AuCl_3$ is reduced by formaldehyde to form colloidal gold sol.

19. (c) **20. (b)**

21. (d): Co^{2+} ion present in group IV is precipitated by H_2S in presence of NH_4OH. Other ions are precipitated as sulphides in presence of dil. HCl in group II.

22. (d): As in every case, normalities of HCl and NaOH are equal, any of the given pair of acid and base can be used.

23. (a): A brown ppt. of MnO_2 will be formed if insufficient quantity of dil. H_2SO_4 is added or H_2SO_4 is not added at all in the titration process. This is due to incomplete reduction of $KMnO_4$.

24. (c) : Nitration of aniline is difficult to carry out with nitrating mixture since $-NH_2$ group gets oxidised which is not required. So, the amino group is first protected by acylation to form acetanilide which is then nitrated to give *p*-nitroacetanilide as a major product.

25. (a)

26. (c) : $\underbrace{Zn^{2+} + Mn^{2+}}_{\text{salt}} \xrightarrow[\text{NaOH}]{\text{Excess}}$

$\underset{\substack{\text{White ppt. soluble}\\ \text{in excess NaOH}\\ \text{(filtrate)}}}{ZnO_2^{2-}}$ + $\underset{\substack{\text{Manganate solution}\\ \text{(slowly changes}\\ \text{into brown ppt.)}}}{MnO_4^{2-}}$

$ZnO_2^{2-} \xrightarrow{\text{HCl}} \underset{\substack{\text{White ppt}\\ \text{(Dissolve in excess of HCl)}}}{ZnCl_2}$

$MnO_4^{2-} \xrightarrow{\text{oxidation}} \underset{\text{(Reddish violet solution)}}{MnO_4^-}$

27. (c) : NaOH + $CuSO_4$ + sodium (*M*), potassium (M_1) tartarate solution is known as Fehling solution and is used for the detection of –CHO group.

28. (b): $E_{cell} = E^\circ_{cell} - \dfrac{0.059}{n}\log\dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

$$E_1 = E^\circ - \frac{0.059}{2}\log\frac{0.01}{1}$$

$$E_1 = E^\circ - \frac{0.059}{2}(-2) = E^\circ + 0.059$$

$$E_2 = E^\circ - \frac{0.059}{2}\log\frac{1}{0.01} = E^\circ - 0.059$$

Hence, $E_1 > E_2$.

29. (d): $Fe(OH)_3$ sol is prepared by shaking $FeCl_3$ with boiling water.

30. (a) : The sol of egg albumin is prepared by shaking white of the egg with cold water.

CBSE BOARD
PRACTICE PAPER 2018

Exam on 13th March

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carry 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

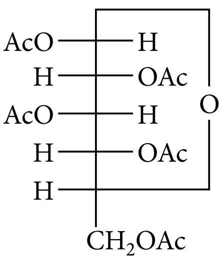
1. Which forces are involved in holding the drugs to the active site of enzymes?

2. Write the name of monomer of PMMA and state one use of it.

3. Does a tetrahedral complex show geometrical isomerism? Give reason.

4. Why $La(OH)_3$ is more basic than $Lu(OH)_3$?

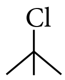
5. Why does compound (*A*) given below not form an oxime?

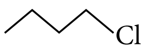


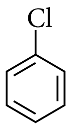
(*A*)

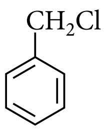
6. The value of $\Delta_f G°$ for the formation of Cr_2O_3 is -540 kJ mol^{-1} and that of Al_2O_3 is -827 kJ mol^{-1}. Is the reduction of Cr_2O_3 possible with Al?

7. In each of the following pairs of compounds, identify the compound which will undergo S_N1 reaction.

(i) 

and 

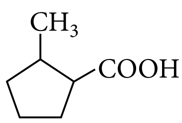
(ii) 

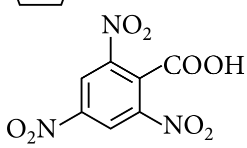
and 

8. Write down the IUPAC names for the following compounds :

(i) $PhCH_2CH_2COOH$

(ii) $(CH_3)_2C{=}CHCOOH$

(iii) 

(iv) 

OR

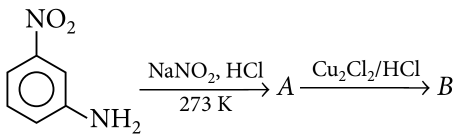
Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6-trimethylcyclohexanone does not. Explain.

9. Physical adsorption decreases with increase in temperature while chemical adsorption first increases and then decreases with increase in temperature. Explain.

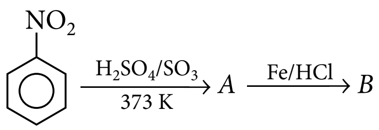
10. An element has a body-centred cubic structure with edge length of 288 pm. The density of the element is 7.2 g cm^{-3}. Calculate the number of atoms in 208 g of the element.

11. Non-ideal solutions exhibit either positive or negative deviations from Raoult's law. What are these deviations and why are they caused? Explain with one example for each type.

12. Identify *A* and *B* in the following reactions :

(i) 

(ii) $CH_3CH_2CH_2Br \xrightarrow{NaCN} A \xrightarrow{LiAlH_4} B$

(iii) 

13. 1 mL of methyl acetate was added to 25 mL of N/2 HCl. 2 mL of reaction mixture were withdrawn from time to time during the progress of the reaction and titrated against standard NaOH solution. Final reading was obtained by completing hydrolysis by boiling the reaction mixture. The following results were obtained :

Time (min) :	0	25	40	61	∞
NaOH used (mL) :	19.24	24.20	26.60	29.50	42.10

Show that reaction is of first order.

14. Answer the following :

(i) Silver crystallises with face-centred cubic unit cell. Each side of this unit cell has a length of 409 pm. What is the radius of silver atom? Assume the atoms just touch each other on the diagonal across the face of the unit cell.

(ii) Explain how we can determine the atomic mass of an unknown metal if density and the dimension of unit cell are known.

OR

In a face-centred lattice of *X* and *Y*, *X* atoms are present at the corners while *Y* atoms are at face centres.

(a) What is the formula of the compound?

(b) What would be the formula of the compound if

(i) one of the *X* atom is missing from a corner in each unit cell.

(ii) one atom of *X* from a corner is replaced by *Z* atom (also monovalent)?

15. The vapour pressure of a dilute aqueous solution of glucose is 750 mm Hg at 373 K. Calculate the molality and mole fraction of the solute.

16. Answer the following questions :

(a) Write down the electronic configuration of the *d*-orbitals of Ti in $[Ti(H_2O)_6]^{3+}$ ion in an octahedral crystal field.

(b) Why is $[Ti(H_2O)_6]^{3+}$ ion coloured? Explain on the basis of distribution of electrons in the *d*-orbitals.

(c) How does the colour change on heating $[Ti(H_2O)_6]^{3+}$ ion?

17. How will you synthesise :

(i) 1-Phenylethanol from a suitable alkene

(ii) Cyclohexylmethanol using an alkyl halide by S_N2 reaction

(iii) Pentan-1-ol using a suitable alkyl halide?

18. For the reaction, $2NO + Cl_2 \rightarrow 2NOCl$ at 300 K following data is obtained :

Expt. No.	Initial concentration ($mol\ L^{-1}$)		Initial rate ($mol\ L^{-1}\ s^{-1}$)
	[NO]	[Cl_2]	
1.	0.010	0.010	1.2×10^{-4}
2.	0.010	0.020	2.4×10^{-4}
3.	0.020	0.020	9.6×10^{-4}

Write rate law of the reaction. What is the order of the reaction? Also calculate the specific rate constant.

19. A white crystalline compound *X* is heated with $K_2Cr_2O_7$ and conc. H_2SO_4, a reddish-brown gas *A* is evolved. On passing *A* into caustic soda solution, a yellow-coloured solution of *B* is obtained. Neutralising the solution *B* with acetic acid on subsequent addition of lead acetate, a yellow precipitate *C* is obtained. Identify *A*, *B*, *C* and *X*.

20. Give reason for the following :

(a) Carboxylic acids do not give characteristic reactions of carboxyl group.

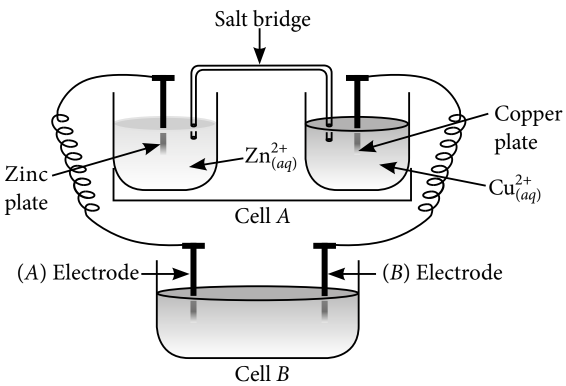
(b) Treatment of benzaldehyde with HCN gives a mixture of two isomers which cannot be separated even by careful fractional distillation.
(c) Sodium bisulphite is used for the purification of aldehydes and ketones.

21. Define the following with one example each
(i) addition polymers,
(ii) condensation polymers, (iii) copolymers.

22. Define the following as related to proteins
(i) Peptide linkage (ii) Primary structure
(iii) Denaturation.

23. A seminar about harmful effects of chlorofluorocarbons (CFCs) was conducted in a school in New Delhi by professor K.G. Sharma who is an ecologist. Professor explained that CFCs were used as refrigerants, propellants for aerosols, as solvents for dry cleaning etc. He explained the destruction of ozone layer by CFCs. He also explained the industrial use of freon 12.
(i) How will freon 12 be manufactured?
(ii) How does CFCs destroy ozone layer?
(iii) What should be done to minimise the harmful effects of CFCs?
(iv) Write two values that are learnt by the students?

24. (a) Consider the figure and answer the following questions.



(i) Cell '*A*' has E_{cell} = 2 V and cell '*B*' has E_{cell} = 1.1 V which of the two cells '*A*' or '*B*' will act as an electrolytic cell? Which electrode reactions will occur in this cell?
(ii) If cell '*A*' has E_{cell} = 0.5 V and cell '*B*' has E_{cell} = 1.1 V then what will be the reactions at anode and cathode?

(b) Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ°_m for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

OR

(a) An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed until all the copper is deposited. The electrolysis is continued for seven more minutes with volume of solution kept at 100 mL and the current at 1.2 amp. Calculate the gases evolved at NTP during the entire electrolysis.
(b) Write down the electrode process when aqueous solutions of following halides are electrolysed:
(i) $NaCl_{(aq)}$ (ii) $NaBr_{(aq)}$ (iii) $NaF_{(aq)}$

25. (a) Write the formula of reagents used in the following reactions :
(i) Bromination of phenol to 2,4,6- tribromophenol
(ii) Hydroboration of propene and then oxidation to propanol.
(b) Arrange the following sets of compounds in the increasing order of their property indicated:
(i) *p*-nitrophenol, ethanol, phenol (acidic character)
(ii) propanol, propane, propanal (boiling point)
(c) Write the mechanism (using curved arrow notation) of the following reaction :

$$CH_3-CH_2-OH \xrightarrow[\text{(ii) } CH_3CH_2OH]{\text{(i) } H^+}$$

OR

(a) How would you obtain the following :
(i) benzoquinone from phenol
(ii) 2-methylpropan-2-ol from methyl magnesium bromide
(iii) propan-2-ol from propene?
(b) Name the different reagents needed to perform the following reactions :
(i) Reduction of phenol to benzene
(ii) Dehydration of propan-2-ol to propene
(iii) Friedel–Crafts alkylation of anisole to *p*-methoxytoluene
(iv) Dehydrogenation of ethanol to ethanal

26. (a) Deduce the shapes of the following on the basis of VSEPR theory.
(i) BrF_3 (ii) I_3^- (iii) IF_7
(b) Explain
(i) $BiCl_3$ is less covalent than PCl_3.
(ii) In HNO_3, N—O bond (121 pm) is shorter than the N—OH bond (140 pm).

OR

(a) Why does the reactivity of nitrogen differ from that of phosphorus?

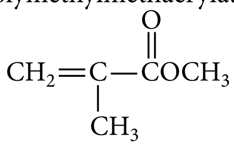
(b) Give at least one example to explain the following properties :

(i) Sulphuric acid is a dibasic acid.
(ii) Sulphuric acid is a dehydrating agent.
(iii) Sulphuric acid is an oxidising agent.

SOLUTIONS

1. Substrates bind to the active site of the enzyme through a variety of interactions such as ionic bonding, hydrogen bonding, van der Waals' interaction or dipole-dipole interaction.

2. PMMA is polymethylmethacrylate, its monomer is



Methylmethacrylate

Use : PMMA is used in making glassy decorative materials.

3. No, because the relative positions of the unidentate ligands coordinated to the central metal atom are the same w.r.t. each other.

4. Due to lanthanoid contraction, the covalent character of hydroxides increases from La^{3+} to Lu^{3+} (Fajan's rule) and hence the basic strength decreases.

5. Glucose pentaacetate (*A*) does not have free —OH at C1, thus cannot be converted to the open chain form to give —CHO group hence, it does not form the oxime.

6. Given that,

$$2Al_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow Al_2O_{3(s)} ; \Delta_f G° = -827 \text{ kJ mol}^{-1} \quad ...(i)$$

$$2Cr_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow Cr_2O_{3(s)} ; \Delta_f G° = -540 \text{ kJ mol}^{-1} \quad ...(ii)$$

On substracting equation (ii) from equation (i), we get

$$2Al_{(s)} + Cr_2O_{3(s)} \rightarrow Al_2O_{3(s)} + 2Cr_{(s)};$$
$$\Delta_r G° = -287 \text{ kJ mol}^{-1}$$

Since $\Delta_r G°$ of this reaction is –ve, therefore, reduction of Cr_2O_3 by Al is possible.

7. (i) Since 3° carbocations are more stable than 1° carbocations, therefore, *tert*-butyl chloride undergoes S_N1 reaction but 1-chlorobutane does not.

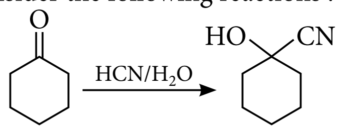
(ii) Benzyl chloride readily forms benzyl carbocation which is stabilized by resonance. Thus, benzyl chloride undergoes S_N1 reaction but chlorobenzene does not undergo S_N1 reaction.

8. (i) 3-Phenylpropanoic acid
(ii) 3-Methylbut-2-enoic acid
(iii) 2-Methylcyclopentanecarboxylic acid
(iv) 2, 4, 6-Trinitrobenzoic acid

OR

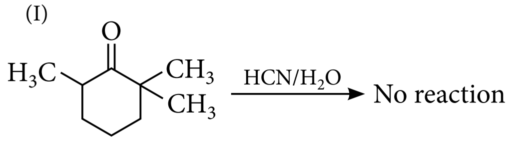
Consider the following reactions :

(a)



(I)

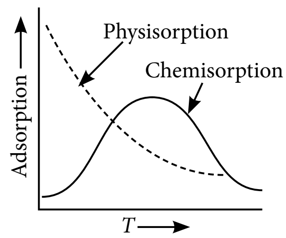
(b)



(II)

In reaction (a), cyanohydrin is formed by the nucleophilic attack of cyanide ion on the carbonyl carbon. But in reaction (b), substrate is sterically hindered due to the presence of the three methyl groups. Hence, the nucleophilic attack of cyanide ion on the carbonyl carbons does not take place. As a result, the reaction does not occur.

9. Physisorption is a type of adsorption in which adsorbate molecules are held to the solid surface (adsorbent) by weak van der Waals' forces. When temperature increases, these forces are weakened resulting in decrease in extent of physisorption. In case of chemisorption, adsorbate molecules are held with adsorbent by chemical bonds with high activation energy. Initial increase in chemisoption is due to heat supplied which acts as activation energy required in chemisorption. But later it decreases due to the exothermic nature of adsorption at equilibrium.



10. Density $d = \frac{MZ}{a^3 N_0}$

where, M = molar mass
d = density = 7.2 g cm^{-3}
N_0 = Avogadro's number = 6.02×10^{23} mol^{-1}
a = edge length = 288 pm = 288×10^{-10} cm
Z = 2 (for *bcc*)

$$M = \frac{dN_0a^3}{Z} = \frac{7.2 \times 6.02 \times 10^{23} \times (288 \times 10^{-10})^3}{2}$$

M = 51.77 g mol^{-1}

Thus, moles of the element in 208 g = $\dfrac{208}{51.77}$ = 4.02

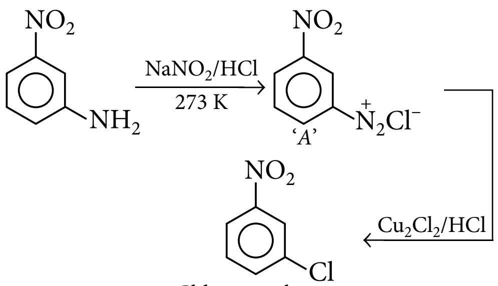
Hence, number of atoms = $4.02 \times N_0$

$= 4.02 \times 6.02 \times 10^{23} = 2.42 \times 10^{24}$ atoms

11. Positive deviation : For non-ideal solution, if the vapour pressure is higher, then it is said to exhibit positive deviation. $A—B$ interactions are weaker than $A—A$ or $B—B$ interactions. Due to this, vapour pressure increases which results in positive deviation. In positive deviation, intermolecular force decreases, volume increases, vapour pressures increases, enthalpy of mixing increases. Therefore, ΔH_{mix} = +ve, ΔV_{mix} = + ve. *e.g.*, ethanol + acetone and carbon disulphide + acetone show positive deviation.

Negative deviation : For non-ideal solution, if the vapour pressure is lower, then it is said to exhibit negative deviation. $A—B$ interactions are stronger than $A—A$ and $B—B$ interactions. Due to this, vapour pressure decreases which results in negative deviation. In negative deviation, intermolecular force increases, volume decreases, vapour pressure decreases and heat is released. Therefore, ΔH_{mix} = –ve, ΔV_{mix} = – ve *e.g.*, phenol + aniline and chloroform + acetone show negative deviation.

12. (i)

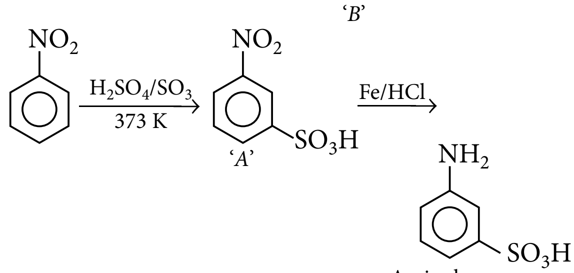


3-Chloronitrobenzene
'B'

(ii) $CH_3CH_2CH_2Br \xrightarrow{NaCN} \underset{\text{'A'}}{CH_3CH_2CH_2C\equiv N} \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2NH_2$

Butanamine
'B'

(iii)



m-Aminobenzene sulphonic acid
'B'

13. Let amount of NaOH used at time $t = 0$ be V_0.

$\therefore$ $V_0 \propto$ HCl present in the mixture

Let amount of NaOH used at any time t be V_t.

$\therefore$ $V_t \propto$ HCl present + acetic acid formed.

$\therefore$ Concentration of acetic acid formed after time t, *i.e.*, $x \propto (V_t - V_0)$

Let amount of NaOH used at $t = \infty$, when reaction is complete, be V_∞.

$\therefore$ $V_\infty \propto$ (HCl present + maximum amount of CH_3COOH formed)

But maximum CH_3COOH formed $\propto$ initial concentration of CH_3COOCH_3

$\therefore$ $a \propto V_\infty - V_0$

$\therefore$ $(a - x) \propto V_\infty - V_0 - (V_t - V_0) \propto V_\infty - V_t$

$\therefore$ Rate law, $k = \dfrac{2.303}{t}\log\dfrac{a}{(a-x)}$ can be written as :

$$k = \frac{2.303}{t}\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

Here, $V_\infty - V_0 = 42.10 - 19.24 = 22.86$ mL

t (minute)	V_t	$V_\infty - V_t$	$k = \dfrac{2.303}{t}\log\dfrac{V_\infty - V_0}{V_\infty - V_t}$
25	24.20	42.10 – 24.20 = 17.90	$k = \dfrac{2.303}{25}\log\dfrac{22.86}{17.90}$ $= 9.785 \times 10^{-3}$ min^{-1}
40	26.60	42.10 – 26.60 = 15.50	$k = \dfrac{2.303}{40}\log\dfrac{22.86}{15.50}$ $= 9.715 \times 10^{-3}$ min^{-1}
61	29.50	42.10 – 29.50 = 12.60	$k = \dfrac{2.303}{61}\log\dfrac{22.86}{12.60}$ $= 9.767 \times 10^{-3}$ min^{-1}

Nearly constant values of rate constant prove that reaction is of first order.

14. (i) As the atoms just touch each other on the diagonal across the face of unit cell, therefore

$b^2 = a^2 + a^2 = 2a^2$

$b = \sqrt{2}a$ ...(i)

Also $b = r + 2r + r = 4r$ ...(ii)

From (i) and (ii), we get

$4r = \sqrt{2}a \Rightarrow r = \dfrac{\sqrt{2}}{4}a$;

$r = \dfrac{1.414 \times 409 \text{ pm}}{4}$

= 144.58 pm

(ii) We can determine the atomic mass of an unknown metal by using the formula of density of its unit cell.

$$d = \frac{Z(\text{No. of atoms per unit cell}) \times M(\text{Atomic mass})}{a^3(\text{Cell edge}) \times N_A \text{ (Avogadro's number)}}$$

By knowing density and dimension of unit cell we can calculate M, the atomic mass of metal for a given unit cell as Z is fixed and N_A is a universal constant.

OR

(a) No. of X atoms in the unit cell $= 8 \times \frac{1}{8} = 1$

No. of Y atoms in the unit cell $= 6 \times \frac{1}{2} = 3$

Formula of the compound = XY_3

(b) (i) If one X atom is missing, no. of X atoms in the unit cell $= \frac{7}{8}$

Formula = $X_{7/8}Y_3$ or X_7Y_{24}

(ii) No. of X atoms $= \frac{7}{8}$, No. of Z atoms $= \frac{1}{8}$

No. of Y atoms = 3.

Formula = $X_{7/8}Y_3Z_{1/8}$ o $X_7Y_{24}Z$

15. Vapour pressure of solution (p_s) at 373 K = 750 mm Hg

Vapour pressure of pure solvent, *i.e.*, water ($p°$) at 373 K = 760 mm Hg

$\therefore$ Lowering in vapour pressure,

$\Delta p = 760 - 750 = 10$ mm Hg

Also, molar mass of glucose ($C_6H_{12}O_6$) = 180 g mol^{-1}

According to Raoult's law,

$$\frac{\Delta p}{p^\circ} = \frac{n_2}{n_1 + n_2} \text{ (Mole fraction of solute)}$$

$\therefore$ Mole fraction of glucose $= \frac{10 \text{ mm}}{760 \text{ mm}} = 0.013$

$\because$ Molality is the number of moles of solute in 1000 g of water.

$\therefore$ Number of moles of water $(n_1) = \frac{1000}{18} = 55.55$ mol

$\therefore \quad \frac{n_2}{55.55 + n_2} = 0.013$

On calculating, we get

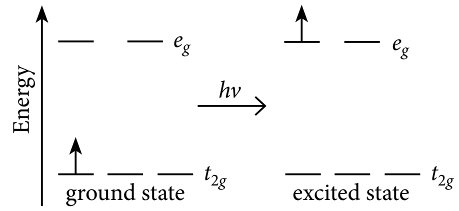
$n_2 = 0.73$ mol/kg or 0.73 m

16. (a) In $[Ti(H_2O)_6]^{3+}$ ion,

Oxidation state of Ti = + 3

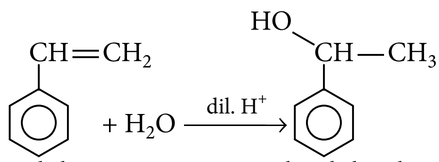
There is only one electron in the d-orbital and its electronic configuration in an octahedral crystal field is $t_{2g}^1 e_g^0$.

(b) Due to d—d transition configuration changes from $t_{2g}^1 e_g^0$ to $t_{2g}^0 e_g^1$ and hence coloured.



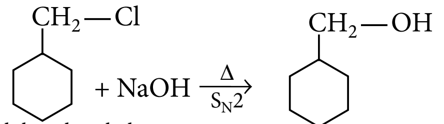
(c) On heating $[Ti(H_2O)_6]^{3+}$ ion becomes colourless as there is no ligand (H_2O) left on heating. In the absence of ligand, crystal field splitting does not occur.

17. (i)



Phenylethene 1-Phenylethanol

(ii)



Cyclohexylmethyl chloride Cyclohexylmethanol

(iii) $CH_3-(CH_2)_3-CH_2-Cl + NaOH \xrightarrow[\Delta]{S_N2,\ \text{hydrolysis}}$ (1-Chloropentane)

$CH_3-(CH_2)_3-CH_2-OH$ (Pentan-1-ol)

18. Let the rate law for the reaction be

Rate = $k[NO]^x[Cl_2]^y$

From Expt. (1), $1.2 \times 10^{-4} = k[0.010]^x[0.010]^y$ ...(i)

From Expt. (2), $2.4 \times 10^{-4} = k[0.010]^x[0.020]^y$ ...(ii)

Dividing Eq. (ii) by Eq. (i),

$$\frac{2.4 \times 10^{-4}}{1.2 \times 10^{-4}} = \frac{[0.020]^y}{[0.010]^y} \Rightarrow 2 = (2)^y \Rightarrow y = 1$$

From Expt. (2), $2.4 \times 10^{-4} = k[0.010]^x[0.020]^y$ ...(iii)

From Expt. (3), $9.6 \times 10^{-4} = k[0.020]^x[0.020]^y$ ...(iv)

Dividing Eq. (iv) by Eq. (iii),

$$\frac{9.6 \times 10^{-4}}{2.4 \times 10^{-4}} = \frac{[0.020]^x}{[0.010]^x} \Rightarrow 4 = 2^x \Rightarrow x = 2$$

Order of reaction = $x + y = 2 + 1 = 3$

Rate law for the reaction is

Rate = $k[NO]^2[Cl_2]$

Considering Eq. (i) again,

$1.2 \times 10^{-4} = k[0.010]^2[0.010]$

$$k = \frac{1.2 \times 10^{-4}}{[0.010]^3} = 1.2 \times 10^2 \text{ mol}^{-2}\text{litre}^2 \text{ sec}^{-1}$$

19. When sodium chloride is heated with $K_2Cr_2O_7$ and conc. H_2SO_4, a reddish-brown gas CrO_2Cl_2 (chromyl chloride) is evolved.

$$4NaCl + K_2Cr_2O_7 + 6H_2SO_4 \longrightarrow$$
$\quad (X) \qquad\qquad\qquad\quad$ (conc.)

$$2KHSO_4 + 4NaHSO_4 + \underset{(A)}{2CrO_2Cl_2}\uparrow + 3H_2O$$

When vapours of chromyl chloride (A) are passed into caustic soda (NaOH), a yellow-coloured solution is obtained due to formation of Na_2CrO_4(B).

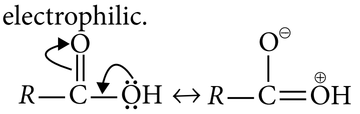
$$\underset{(A)}{CrO_2Cl_2} + 4NaOH \longrightarrow \underset{(B)}{Na_2CrO_4} + 2NaCl + 2H_2O$$

On subsequent addition of lead acetate solution, a yellow precipitate of $PbCrO_4$(C) is obtained.

$$\underset{(B)}{Na_2CrO_4} + (CH_3COO)_2Pb \rightarrow \underset{(C)}{PbCrO_4}\downarrow + 2CH_3COONa$$

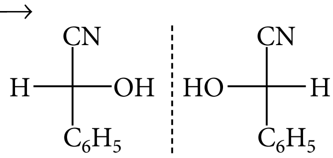
Thus, A is chromyl chloride, B is Na_2CrO_4, C is $PbCrO_4$ and X is a chloride (say, NaCl).

20. (a) Due to resonance, CO group of carboxylic acid is no more electrophilic.



(b) It is because we get two optical isomers which have same physical properties, therefore, cannot be separated by fractional distillation.

$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H + HCN \longrightarrow$$



$d(+) \qquad l(-)$

Benzaldehyde cyanohydrin

(c) Aldehydes and ketones form addition products with $NaHSO_3$ whereas impurities do not. On hydrolysis, we get pure aldehydes and ketones back.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + NaHSO_3 \rightleftharpoons CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-SO_3Na$$

$$\xrightarrow{H_2O/H^+} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + NaHSO_3$$

21. (i) Addition polymers : The polymers formed by the addition reaction of a large number of unsaturated monomers are called addition polymers. *e.g.*, Polyethene.

(ii) Condensation polymers : The polymers formed by the condensation of two or more bifunctional monomers are called condensation polymers. *e.g.*, Nylon 6, 6.

(iii) Copolymers : The polymers made by addition polymerisation from two different compounds are known as copolymers. *e.g.*, Buna-S.

22. (i) Peptide Linkage : Proteins are the polymers of α-amino acids which are connected to each other by peptide bond or peptide linkage. Chemically, peptide linkage is an amide formed between —COOH group and —NH_2 group. The reaction between two molecules of similar or different amino acids, proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond —CO—NH—.

(ii) Primary Structure : Proteins may have one or more polypeptide chains. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be the primary structure of that protein. Any change in this primary structure *i.e.*, the sequence of amino acids creates a different protein.

(iii) Denaturation : Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to physical change like change in temperature or chemical change in pH, the hydrogen bonds are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. This is called denaturation of protein.

During denaturation 2° and 3° structures are destroyed but 1° structure remains intact. The coagulation of egg white on boiling is a common example of denaturation of protein.

23. (i) Freon 12 is manufactured from carbon tetrachloride by Swarts reaction.

$$3CCl_4 + 2SbF_3 \xrightarrow{SbCl_5} \underset{\text{Freon 12}}{3CCl_2F_2} + 2SbCl_3$$

(ii) $NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

$CF_2Cl_2 \rightarrow CF_2Cl^\bullet + Cl^\bullet$ (In presence of light)

$CFCl_3 \rightarrow CFCl_2^\bullet + Cl^\bullet$

$Cl^\bullet + O_3 \rightarrow ClO^\bullet + O_2$

$ClO^\bullet + O \rightarrow Cl^\bullet + O_2$

Solution Senders of Chemistry Musing

Set - 55

- Ashwini Mukherjee, West Bengal

Set - 54

- Varun Gowda, Karnataka
- Anushka Singh, Rajasthan

(iii) CFCs must be replaced by other compounds which are not harmful like natural refrigerant, isobutane can be used in domestic refrigerator.

(iv) Concern and environment conservation are values learnt by the students through this seminar.

24. (a) (i) Cell *B* will act as electrolytic cell as it has lower emf.

The electrode reaction will be

$Zn^{2+} + 2e^- \longrightarrow Zn$ (Cathode)

$Cu \longrightarrow Cu^{2+} + 2e^-$ (Anode)

(ii) With the values of emf, cell *B* will act as galvanic cell due to higher emf and will push electrons into cell *A*.

The electrode reactions will be

$Zn \longrightarrow Zn^{2+} + 2e^-$ (Anode)

$Cu^{2+} + 2e^- \longrightarrow Cu$ (Cathode)

(b) $\Lambda_m^c = \dfrac{\kappa \times 1000}{C} = \dfrac{(7.896 \times 10^{-5}) \times 1000}{0.00241}$

$= 32.76\ S\ cm^2\ mol^{-1}$

$\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^o} = \dfrac{32.76}{390.5} = 8.4 \times 10^{-2}$

$K_a = \dfrac{C\alpha^2}{1-\alpha} = \dfrac{0.00241 \times (8.4 \times 10^{-2})^2}{1-(8.4\times 10^{-2})} = 1.86 \times 10^{-5}$

OR

(a) 0.4 g of $Cu^{2+} = \dfrac{0.4}{31.75} = 0.0126$ g equivalent

At the same time, the oxygen deposited at anode

$= 0.0126$ g equivalent $= \dfrac{8}{32} \times 0.0126 = 0.00315$ g mol

After the complete deposition of copper, the electrolysis will discharge hydrogen at cathode and oxygen at anode.

The amount of charge passed $= 1.2 \times 7 \times 60$

$= 504$ coulomb

So, oxygen liberated $= \dfrac{1}{96500} \times 504 = 0.00523$ g equivalent

$= \dfrac{8}{32} \times 0.00523 = 0.001307$ g mol

Hydrogen liberated $= 0.00523$ g equivalent

$= \dfrac{1}{2} \times 0.00523 = 0.00261$ g mol

Total gases evolved $= (0.00315 + 0.001307 + 0.00261)$ g mol $= 0.007067$ g mol

Volume of gases evolved at NTP

$= 22400 \times 0.007067$ mL $= 158.3$ mL

(b) (i) $2H^+ + 2e^- \longrightarrow H_2\uparrow$ (Cathode)

$2Cl^- \longrightarrow Cl_2 + 2e^-$ (Anode)

(ii) $2H^+ + 2e^- \longrightarrow H_2\uparrow$ (Cathode)

$2Br^- \longrightarrow Br_2 + 2e^-$ (Anode)

(iii) $2H^+ + 2e^- \longrightarrow H_2\uparrow$ (Cathode)

$2OH^- \longrightarrow H_2O + \dfrac{1}{2}O_2 + 2e^-$ (Anode)

25. (a) (i) Br_2/H_2O

(ii) BH_3 in THF/H_2O_2

(b) (i) *p*-Nitrophenol > phenol > ethanol

(ii) Propanol > propanal > propane

(c) $CH_3-CH_2-\ddot{O}H \xrightarrow{H^+}$

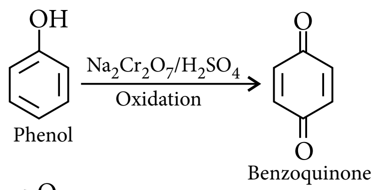
$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow[\substack{-H_2O \\ S_N2\ \text{mechanism}}]{CH_3-CH_2-\ddot{O}H}$

$CH_3-CH_2-\overset{+}{\underset{H}{O}}-CH_2-CH_3$

$\big\downarrow -H^+$

$CH_3-CH_2-O-CH_2-CH_3$

OR

(a) (i) 

(ii) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3MgBr \longrightarrow \left[CH_3-\overset{\overset{-\ +}{O}MgBr}{\underset{CH_3}{C}}-CH_3\right] \xrightarrow{H_2O} CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3$

2-Methylpropan-2-ol

(iii) $\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[H_2O]{H_2SO_4} \underset{\text{Propan-2-ol}}{CH_3-\overset{OH}{CH}-CH_3}$

(b) (i) Zinc dust

(ii) Concentrated H_2SO_4

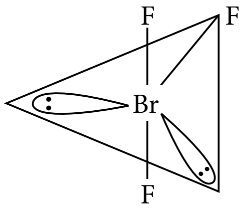
(iii) CH_3Cl and $AlCl_3$ (anhyd.)

(iv) Cu/573 K

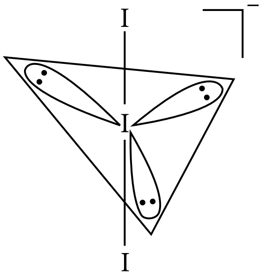
26. (a) (i) $\mathbf{BrF_3}$ **:** This molecule has two lone pairs and three bond pairs.

To minimise the lone pair-lone pair and lone pair-bond pair repulsions, these two lone pairs occupy the equatorial positions. Also, axial fluorine atoms will be bent towards the equatorial fluorine atom in order to minimise lone pair-lone pair repulsions.

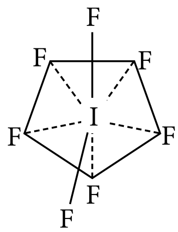
Shape : slight bent T-shaped



(ii) Triiodide ion (I_3^-) : I_3^- ion is made up of an I_2 molecule with an I^- bonded to it by means of a coordinate bond in which I_2 is lone pair acceptor (Lewis acid) and I^- is lone pair donor (Lewis base). There are two bond pairs and three lone pairs in the outer shell of central atom. To minimise the repulsive forces the three lone pairs occupy the equatorial position. The ion is therefore linear in shape with a bond angle of exactly 180°.



(iii) Iodine heptafluoride (IF_7) : This is the only common example of a non-transition element using seven orbitals for bonding giving a pentagonal bipyramidal shape.



(b) (i) By Fajan's rule,

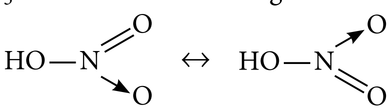
- smaller the size of cation
- larger the size of anion
- larger the charge

then larger the polarising power and hence, greater the covalent character.

$Bi^{3+} > P^{3+}$ (size)

Charges are identical, anions are same. Thus, polarising power is decided by size of cation. Thus, $BiCl_3$ is less covalent than PCl_3.

(ii) HNO_3 exists as two resonating structures.



(N—O) bond is resonance stabilised and it has average bond length between = and — bond, while (N—OH) bond is purely single. Thus, (N—O) bond length is shorter than the (N—OH) bond.

OR

(a) Molecular nitrogen exists as a diatomic molecule having a triple bond between the two nitrogen atoms (N≡N). The bond dissociation energy is very high (945 kJ mol^{-1}). Thus, under ordinary conditions, nitrogen behaves as inert gas. On the other hand, white or yellow phosphorus exists as a tetratomic molecule (P_4) having single bonds. The bond dissociation energy of P—P bond is low (213 kJ mol^{-1}). Thus, phosphorus is much more reactive than nitrogen.

(b) (i) H_2SO_4 forms two series of salts, *i.e.*, both the hydrogen atoms are replaceable.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-}$$

$$H_2SO_4 + NaOH \longrightarrow \underset{\text{Sodium hydrogen sulphate (Acidic salt)}}{NaHSO_4} + H_2O$$

$$H_2SO_4 + 2NaOH \longrightarrow \underset{\text{Sodium sulphate (Normal salt)}}{Na_2SO_4} + 2H_2O$$

(ii) H_2SO_4 has great affinity for water molecules and hence, acts as a dehydrating agent.

$$\underset{\text{Formic acid}}{HCOOH} \xrightarrow{\text{Conc. } H_2SO_4} H_2O + CO$$

(iii) H_2SO_4 oxidises metals, non-metals and other compounds.

$$\overset{0}{Cu} + 2H_2SO_4(\text{conc.}) \longrightarrow \overset{+2}{Cu}SO_4 + SO_2 + 2H_2O$$

$$\overset{0}{S} + 2H_2SO_4 \longrightarrow 3\overset{+4}{S}O_2 + 2H_2O$$

◇◇

EXAM CORNER 2018

Exam	Date
VITEEE	4th to 15th April
JEE Main	8th April (Offline), 15th & 16th April (Online)
SRMJEEE	16th to 30th April
Karnataka CET	18th & 19th April
WBJEE	22nd April
Kerala PET	23rd & 24th April
NEET	6th May
MHT CET	10th May
COMEDK (Engg.)	13th May
AMU (Engg.)	13th May (Revised)
BITSAT	16th to 31st May
JEE Advanced	20th May
AIIMS	27th May
JIPMER	3rd June

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